# High Pressure Phase Equilibria in the Carbon Dioxide + Pyrrole System

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High Pressure Phase Equilibria in the Carbon Dioxide + Pyrrole System

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# LIST OF SYMBOLS AND ABBREVIATIONS

| | |
|---|---|
| A | Area of Gibbs Energy of Mixing Curve |
| $A_{\infty}^{E}$ | Excess Helmholtz Energy at Infinite Pressure |
| a, b, c | Equation of State Constants |
| C | Constant Dependent from Wong-Sandler mixing rule |
| $C_1$ | Parameter in Huron – Vidal Mixing Rule |
| CSvdW | **C**arnahan-**S**taring-**v**an **d**er **W**aals |
| EOS | **E**quation **o**f **S**tate |
| $\hat{f}_i^{\,L}$ , $\hat{f}_i^{\,V}$ | Fugacity of Component i in Liquid Phase, and Vapor Phase |
| F | Parameter in PT EOS |
| $G_{\infty}^{E}$ | Excess Gibbs Energy at Infinite Pressure |
| $\Delta G_m$ | Gibbs Energy of Mixing |
| HV | **H**uron – **V**idal |
| $k_{ij}$ | Binary Interaction Parameter |
| $l_{ij}$ | Binary Interaction Parameter |
| LCEP | **L**ower **C**ritical **E**nd **P**oint |
| LL | **L**iquid – **L**iquid |
| LLE | **L**iquid – **L**iquid **E**quilibrium |
| LLV | **L**iquid – **L**iquid – **V**apor |
| LV | **L**iquid – **V**apor |
| m | Parameter in Various EOS |

| | |
|---|---|
| MKP | **M**athias – **K**lotz – **P**rausnitz |
| $n_i$ | Moles of Component i |
| P | Pressure (Absolute) |
| $P_c$ | Critical Pressure |
| PEA | **P**hase **E**quilibrium **A**nalyzer |
| PR | **P**eng – **R**obinson |
| PRSV | **P**eng-**R**obinson-**S**tryjek-**V**era |
| PT | **P**atel – **T**eja |
| R | Gas Constant |
| RTD | **R**esistive **T**hermal **D**evice |
| SCF | **S**uper **C**ritical **F**luid |
| SRK | **S**oave – **R**edlich – **K**wong |
| T | Temperature (Absolute) |
| $T_c$ | Critical Temperature |
| $T_R$ | Reduced Temperature |
| UCEP | **U**pper **C**ritical **E**nd **P**oint |
| UCST | **U**pper **C**ritical **S**olution **T**emperature |
| u | Equation of State Dependent Constants |
| vdW | **v**an **d**er **W**aals |
| V | Total Volume |
| VLE | **V**apor **L**iquid **E**quilibrium |
| w | Equation of State Dependent Constants |

| | |
|---|---|
| $x_i$ | Mole Fraction of Component i in the Liquid Phase |
| $y_i$ | Mole Fraction of Component i in the Vapor Phase |
| $\alpha$ | Substance Dependent Parameter in Equation of State |
| $\zeta$ | Compressibility Factor |
| $\eta$ | Packing Fraction in CSvdW EOS |
| $\kappa_1$ | Adjustable Parameter in PRSV EOS |
| $\nu$ | Molar Volume |
| $\phi$ | Dimensionless Gibbs Energy of Mixing |
| $\hat{\phi}_i^L$ , $\hat{\phi}_i^V$ | Fugacity Coefficient of Component i in liquid phase, and vapor phase |
| $\omega$ | Acentric Factor |
| $\Omega_a, \Omega_b, \Omega_c$ | Substance Specific Constants |

## SUMMARY

The objectives of this work are to measure phase equilibria in the carbon dioxide + pyrrole system and to correlate and predict the phase behavior of this system with a thermodynamic model. This binary system is of interest due to the growing applications of supercritical carbon dioxide as a solvent or reaction medium for pyrrole. Polypyrrole is an electrically conducting polymer of interest in a number of applications such as anti-static coatings. Pyrrole has also been used as a reactant in enzymatic reaction. Knowledge of the phase behavior of carbon dioxide + pyrrole system is therefore necessary for evaluating optimal conditions and feasibility of such applications.

Phase equilibria in the carbon dioxide + pyrrole system were measured at 313 K, 323 K, and 333 K using a synthetic method. Liquid-vapor (LV) phase behavior and liquid-liquid (LL) phase behavior were observed. The pressure in the experiments ranged from 84 to 151.1 bar. The Patel-Teja equation of state and the Mathias-Klotz-Prausnitz mixing rule with two temperature independent parameters was able to correlate the phase equilibrium data satisfactorily and was used to predict the phase behavior at other temperatures. A pressure-temperature diagram was then constructed from these calculations and suggests that the carbon dioxide + pyrrole system exhibit type IV phase behavior in the classification of Scott and van Konynenburg.

# CHAPTER 1

# INTRODUCTION

Supercritical carbon dioxide ($scCO_2$) is well known as a 'green' alternative for organic solvents since its use for coffee and tea decaffeination in the early 1980s (Teja and Eckert 2000). Besides its nontoxic nature, carbon dioxide is inexpensive, nonflammable, extensively available, and has a broad range of dissolving power, especially in the supercritical region (critical point: 31.1 °C, 73.8 bar). Supercritical $CO_2$ exhibits gas-like transport properties of diffusivity and viscosity, as well as low surface tension that allow facile penetration into microporous materials.

Various applications of $scCO_2$ can be found in broad range of areas such as natural product extractions (Mukhopadhyay 2000), dyeing and cleaning of fiber and textiles (Kazarian et al. 1999), purifications and crystallizations of pharmaceuticals (Kaiser et al. 2001), catalysis and chemical synthesis (Leitner 2003), minerals recovery (Debelak et al. 2003), and polymer synthesis and processing (Cooper 2000).

The phase behavior of mixtures in which carbon dioxide is the solvent is of interest in the design of supercritical processes. In particular, the feasibility and optimal conditions for such processes can be determined if the phase behavior is known. Considerable effort has therefore been devoted to the measurement of such behavior in carbon dioxide + solute systems, as reviewed in Fornari et al. (1990), Dohrn and Brunner (1995), and Christov and Dohrn (2002).

The binary system carbon dioxide + pyrrole is of particular interest in this study because pyrrole is the monomer for polypyrrole, which is an industrially important

electrically conducting polymer (Abbett et al. 2003b; Kerton et al. 1997; Kurosawa 2004; Tang et al. 2002). The carbon dioxide + pyrrole system has also been used in enzymatic catalytic reactions by Matsuda et al.(2001) and Matsuda et al. (2004). Understanding the phase behavior of this system can therefore provide important information regarding the role of supercritical carbon dioxide as a solvent or a reaction medium in diverse applications.

One objective of this work was to measure phase equilibria in the carbon dioxide + pyrrole system at temperatures of interest in supercritical processing, such as 313 K, 323 K, and 333 K. Prior to this study, the only information available concerning the solubility of pyrrole in supercritical carbon dioxide was the comment by Dange et al. (1985) that pyrrole is miscible in all proportions in dense carbon dioxide at 298.15 K and 305.15 K at 172.4 bar. Kerton et al. (1997) also reported that pyrrole is soluble in supercritical carbon dioxide at 353.15 K and 150 bar, and at 423.15 K and 80 bar. Neither of these studies, however, measured compositions of carbon dioxide + pyrrole mixtures in equilibrium. Therefore, studies of the pressure-temperature-composition behavior are of considerable interest.

The second objective of this work was to correlate the phase equilibrium data with an equation of state so that the behavior of this system at other conditions may be predicted or inferred. The thermodynamic model would provide more insight into the phase behavior of carbon dioxide + pyrrole which would lead to better process design and improvement. Fewer experiments would be required in order to obtain a comprehensive understanding of the phase behavior of the carbon dioxide + pyrrole system.

# CHAPTER 2

# BACKGROUND

This chapter reviews available measurement techniques for high pressure fluid phase equilibria, and discusses a classification of phase diagrams for binary mixtures. The thermodynamic models used in this thesis are also reviewed.

## 2.1 Measurement of High Pressure Fluid Phase Equilibria

Several experimental methods have been developed for the measurement of high pressure fluid phase equilibria. The methods can be divided into analytical or direct sampling methods, and synthetic or indirect methods, depending on how composition is measured. Comprehensive reviews of such methods can be found in Christove and Dohrn (2002), Dohrn and Brunner (2002; 1995), Fornari et al.(1990).

### 2.1.1 Analytical Methods

Analytical or direct sampling methods can be subdivided into static, recirculation, and flow methods depending on the technique used for equilibration of the phases. The static method employs a number of configurations to facilitate equilibration. The schematic of this method is shown in Figure 2.1. A vapor-liquid mixture is kept in the equilibrium cell which is temperature and pressure controlled. An agitation or stirring device can be used to enhance the attainment of equilibrium. After equilibrium is reached, small samples of both the vapor and liquid phase are withdrawn, and their composition is analyzed. Despite the simplicity of this static method, care must be taken not to cause a serious disturbance of the equilibrium condition while sampling.

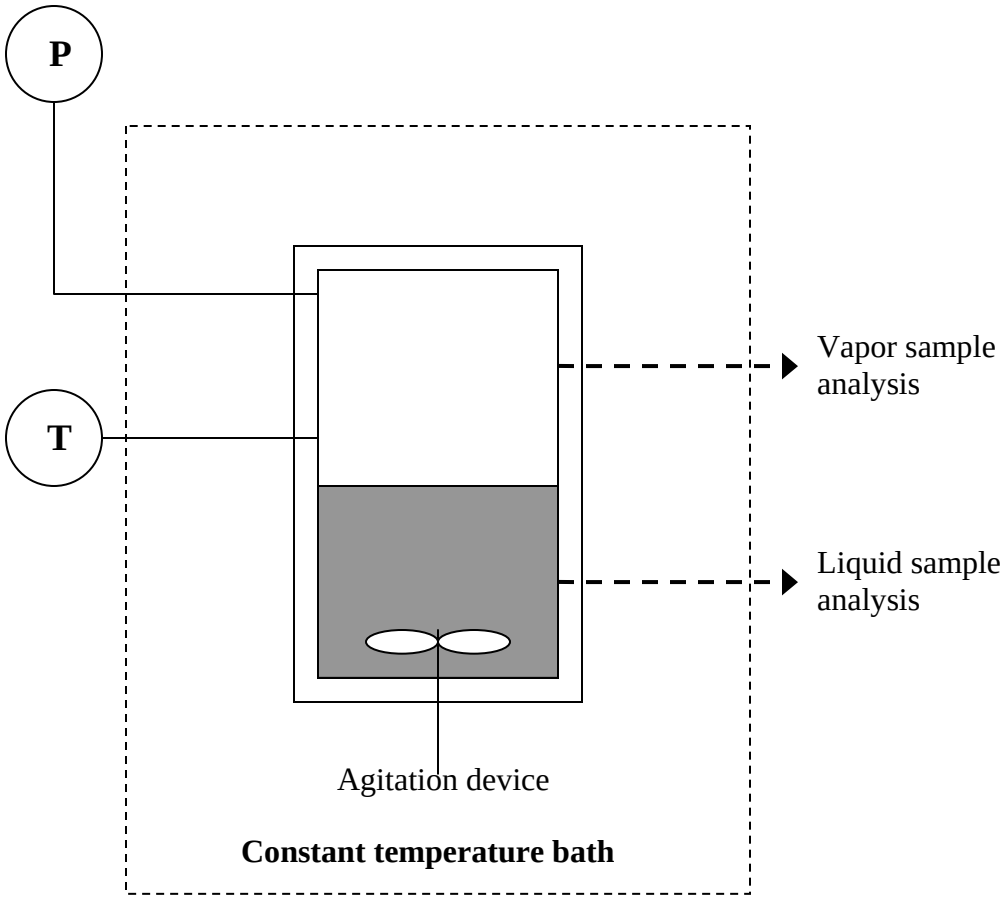


**Figure 2.1:** Static Method

The static analytical methods have been used in various phase equilibrium measurements (Mühlbauer and Raal 1991; Nakayama et al. 1987; Wagner and Wichterle 1987; Zimmerman and Keller 1989) A review of some static analytical methods used in the literature can be found in Arai et al.(2002), Raal and Mühlbauer (1998).

The second method is the recirculation method shown in Figure 2.2. This method utilizes a closed vessel similar to the static method, but both vapor and liquid phases are countercurrently recirculated in order to provide better mixing of the phases and to ensure the attainment of equilibrium. The analysis of the composition of both phases is accomplished by taking a small amount of the circulating phases through sample valves which are connected on-line to an analytical device. Undesirable pressure gradients across the equilibrium cell caused by the circulating pump have to be avoided (Raal and Muhlbauer 1998). A detailed description of the recirculation method can be found in Jennings (1991), Yu et al.(1992), Beier et al. (2003), and Kodama et al. (2004).

The flow method is shown in Figure 2.3. Components are introduced into a static mixer using high pressure pumps, and then separated into a liquid and vapor phase in an equilibrium cell. A liquid or heavy phase is continuously withdrawn from the bottom of the equilibrium cell while a vapor or light phase is withdrawn from the top of the cell. Both phases are then depressurized, accumulated, and analyzed. Sampling of the phases does not disturb the equilibrium and large sample sizes can be generated for analysis when the components are in dilute concentrations (Christov and Dohrn 2002). Examples of phase equilibrium measurement using the flow method can be found in Suzuki et al.(1991),Vandana and Teja (1995) , Huruki et al.(2000), and Shimoyama et al. (2002).

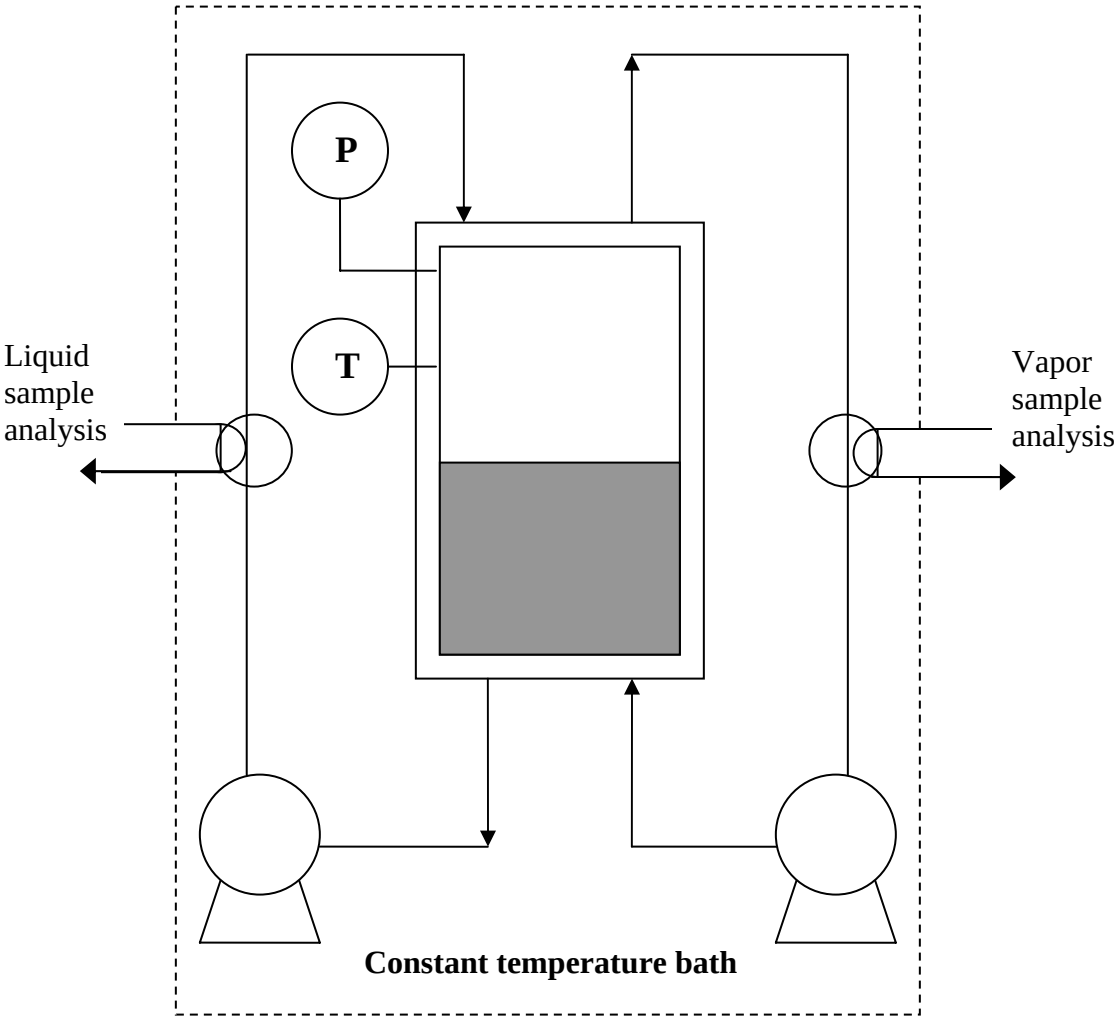


**Figure 2.2:** Recirculation Method

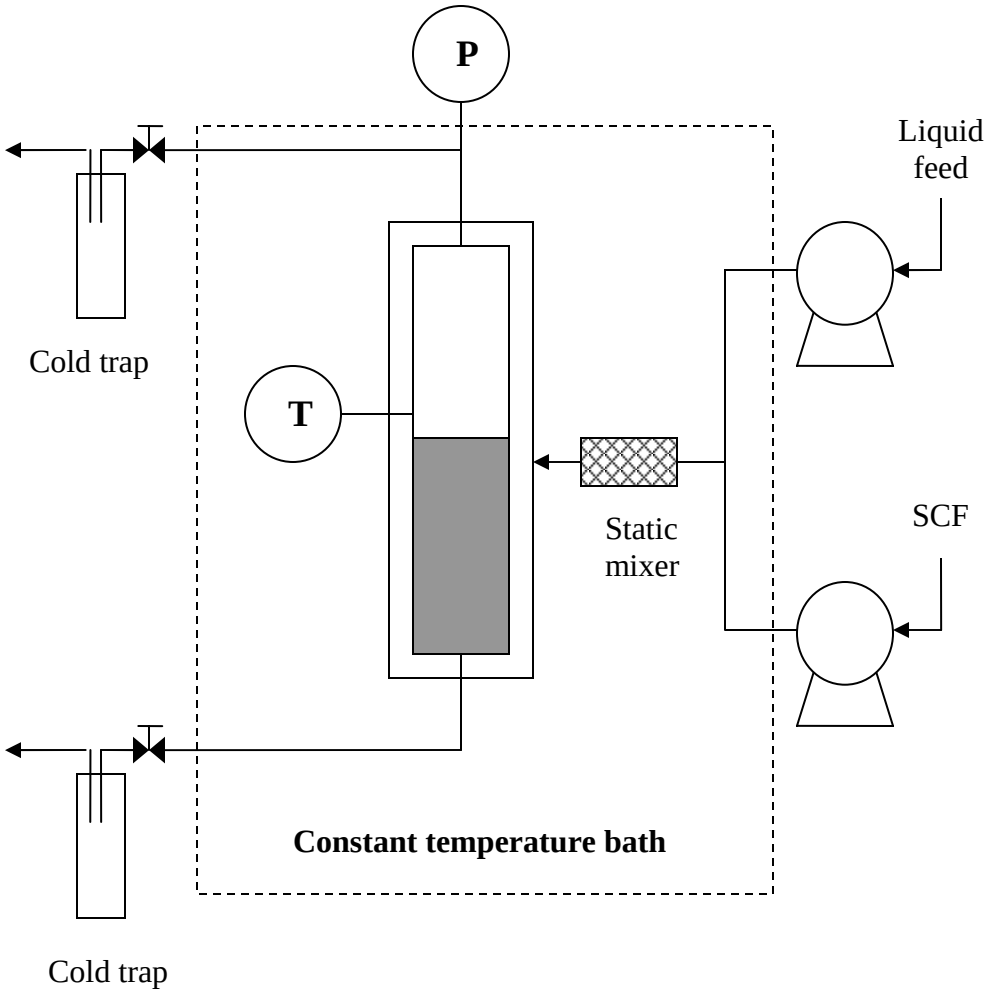


**Figure 2.3:** Flow Method

### 2.1.2 Synthetic Methods

In synthetic methods, a mixture of known composition is pressurized in an equilibrium vessel to obtain a homogeneous phase at constant temperature. Phase equilibrium data can be obtained by varying the volume inside the equilibrium vessel until the formation of a new phase is detected either by visual observation or by changes in physical properties (Abedi et al. 1999). Thus, there is no disturbance of equilibrium from sampling of the phases.

Synthetic methods can be used when the coexisting phases have similar density (Zhang and Kiran 2003), such as in the critical region (Christov and Dohrn 2002). However, visual observation of new phase formation is difficult for an isooptic system, where the coexisting phases have approximately the same refractive index (Ruiz et al. 1986). The use of synthetic method for multicomponent systems is not practical since the tie lines cannot be determined without additional experiments (Costa et al. 1996).

A major advantage of synthetic methods is that complicated sampling and analytical devices are not required. Thus, this method was chosen in this work to measure phase equilibrium. A detailed description of the method is given in chapter 3. Some other examples of high pressure phase behavior measurement using synthetic methods can be found in Sato et al.(1998), Byun and Shin(2003), Kodama et al.(2004), Lazzaroni et al.(2004), and Tsuja et al.(2004).

## 2.2 Classification of Phase Diagrams for Binary Mixtures

A wide variety of phase behavior can be found at high pressures as described by Scott and van Konynenburg (1970). These authors categorized binary phase behavior into

six types on pressure-temperature diagrams. Five of these types of diagram can be generated with the van der Waals equation of state and are shown in Figure 2.4.

Type I phase behavior is characterized by a continuous critical locus between the two pure component critical points, and no liquid-liquid immiscibility (Figure 2.4a). This type of phase behavior usually occurs when the two components of the mixture have similar molecular size and interaction energies, or when the two component critical properties are of comparable magnitude (McHugh and Krukonis 1994). Some examples of binary mixtures that exhibit type I phase behavior include methane – ethane (Wei et al. 1995), carbon dioxide – hexane (Li et al. 1981), and carbon dioxide – toluene (Ng and Robinson 1978).

Type II phase behavior, as shown in Figure 2.4b, is similar to type I behavior except that liquid-liquid immiscibility appears at low temperatures. A liquid-liquid-vapor line can also be found in the diagram along which three phases (two liquid and a vapor) are in equilibrium. The end of the LLV line is called the UCEP (upper critical end point) where the two liquid phases merge into one liquid phase. The LL (liquid-liquid) line in the diagram is called a UCST (upper critical solution temperature) line where two liquids critically merge to form a single liquid phase as the system temperature is raised. An example of this type of phase behavior is carbon dioxide – 1-butanol (Lam et al. 1990)

Type III phase behavior usually occurs for mixtures with large immiscibility such as water – *n*-alkane mixtures (Rowlinson and Swinton 1982). The LL line moves up to higher temperatures and finally interferes with the vapor-liquid critical curve, which results in a discontinuous critical curve. This critical curve, which starts at the critical

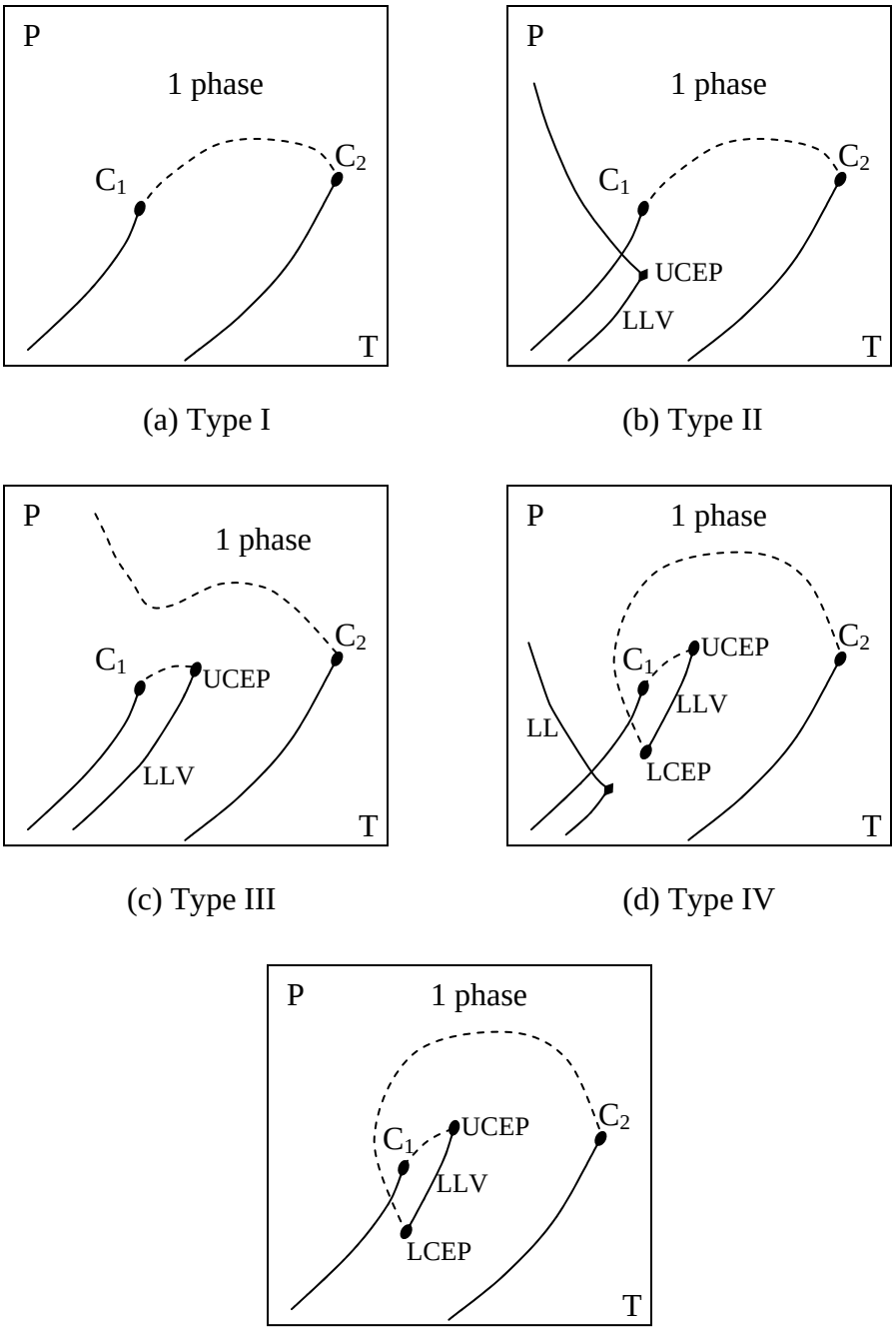


**Figure 2.4**: Five types of binary phase behavior as determined from the van der Waals equation of state. $C_1$ and $C_2$ are the critical points of more and less volatile components, respectively.

point of the less volatile component, can exhibit positive or negative slope and extends to higher pressures while gradually changing its nature from LV to LL (Figure 2.4c). The other critical curve goes from the critical point of the more volatile component to the UCEP. In this case, the UCEP is a point where the liquid and vapor phase critically merge to form a single fluid phase in the presence of another liquid phase. Some examples of type III phase behavior are ethane – methanol (Ishihara et al. 1998), carbon dioxide – n-hexadecane (Hoelscher et al. 1989), and carbon dioxide – 1-hexanol (Beier et al. 2003).

Type IV and type V phase behavior are similar and are shown in Figure 2.4d and Figure 2.4e, respectively. Type IV has a UCST line similar to type II at lower temperatures. Type V does not have a UCST line although it is likely that most type V systems would show this additional immiscibility if the onset of solid phases did not intervene (Rowlinson and Swinton 1982). The characteristic of this type of phase behavior is that the LLV region is located very close to the critical point of the more volatile component. The first branch of the critical mixture curve starts from the critical point of the more volatile component to the UCEP. The other branch goes from the critical point of the less volatile component, gradually changing its nature from LV to LL, and intersects the LLV line at an LCEP (lower critical end point). Type IV (or type V) phase behavior is usually observed when the critical properties of the two components differ substantially. This can be attributed to large differences in molecular size, structure, or intermolecular forces. For example, binary hydrocarbon mixtures with large size differences exhibit type V phase behavior. The binary mixtures of ethane with ethanol, 1-propanol, and 1-butanol (Kuenen and Robson 1899) show type IV behavior since the

alcohol-alcohol hydrogen bonding interactions overcome alcohol – hydrocarbon interactions. Other similar systems include ethylene – 1-propanol (Kodama et al. 2004), carbon dioxide – nitrobenzene (Kohnstamm and Reeders 1913), and carbon dioxide – 2-nitrophenol (Scheffer and Smittenberg 1933).

### 2.3 Thermodynamic Modeling of High-Pressure Fluid Phase Equilibria

A vapor is in equilibrium with a liquid phase when both are at the same temperature T and pressure P, and when the fugacity of any component *i* in the vapor phase is equal to that in the liquid phase. Thus:

$$\hat{f}_i^V = \hat{f}_i^L \tag{2.1}$$

The above equation can be expressed in terms of fugacity coefficients $\hat{\phi}_i$ as follows,

$$y_i \hat{\phi}_i^V P = x_i \hat{\phi}_i^L P \tag{2.2}$$

where $y_i$ and $x_i$ are the mole fractions of component *i* in the vapor and liquid phase, respectively. Alternatively, the liquid phase can be represented by an activity coefficient model. However, the use of different approaches for calculating fugacity coefficients for each phase may lead to a discontinuity as the critical region of the mixture is approached (Poling et al. 2001). Fugacity coefficients of vapor and liquid phases can be calculated from the following thermodynamic relationship:

$$\ln \hat{\phi}_i = \frac{1}{RT} \int_V^{\infty} \left[ \left( \frac{\partial P}{\partial n_i} \right)_{T,V,n_{i \neq j}} - \frac{RT}{V} \right] dV - \ln \left( \frac{Pv}{RT} \right) \tag{2.3}$$

where $R$ is the gas constant, V is the total volume of the phase, $v$ is the molar volume of the phase, and $n_i$ and $n_j$ are the moles of components $i$ and $j$, respectively. A single equation of state can now be used to calculate fugacities.

### 2.3.1 Equations of State

The van der Waals equation of state (vdW EOS), proposed in 1873, was the first equation capable of representing vapor-liquid coexistence (Rowlinson 1988):

$$P = \frac{RT}{v - b} - \frac{a}{v^2} \tag{2.4}$$

The van der Waals equation is a cubicequation of state composed of repulsive and attractive contributions of intermolecular interactions. It was demonstrated by Scott and van Konynenburg (1980) that the vdW EOS can quantitatively predict most types of phase equilibria exhibited by binary mixtures. However, the calculations are seldom quantitatively accurate. Therefore, many modifications of the vdW EOS have been proposed. Some of the important equations are discussed below.

For high pressure phase equilibria, the most widely used equations are the Soave-Redlich-Kwong equation (SRK: Soave 1972b) and the Peng-Robinson equation (PR: Peng and Robinson 1976). SRK EOS is one of the first simple cubic EOS based on vdW

EOS to obtain wide application in phase equailibrium calculations. The SRK EOS has the following form:

$$P = \frac{RT}{v-b} - \frac{a[T]}{v(v+b)} \tag{2.5}$$

where

$$a[T] = 0.4274(\frac{R^2 T_c^{\,2}}{P_c})\alpha[T_R] \tag{2.6}$$

$$\alpha[T_R] = \left\{1 + m[1 - T_R^{\,0.5}]\right\}^2 \tag{2.7}$$

$$m = 0.480 + 1.57\omega - 0.176\omega^2 \tag{2.8}$$

$$b = 0.08664\frac{RT_c}{P_c} \tag{2.9}$$

The PR EOS has the form:

$$P = \frac{RT}{v-b} - \frac{a[T]}{v(v+b)+b(v-b)} \tag{2.10}$$

where

$$a[T] = 0.45724(\frac{R^2 T_c^{\,2}}{P_c})\alpha[T_R] \tag{2.11}$$

$$\alpha[T_R] = \left\{1 + m[1 - T_R^{\,0.5}]\right\}^2 \tag{2.12}$$

$$m = 0.37464 + 1.5422\omega - 0.26922\omega^2 \tag{2.13}$$

$$b = 0.07780\frac{RT_c}{P_c} \tag{2.14}$$

The advantage of using SRK and PR equations of state is their ability to accurately represent phase equilibria using only critical properties and acentric factors as characteristic pure-component parameters. However, the SRK and PR EOS have limited capability in predicting saturated liquid densities, and are not accurate for highly polar systems.

Stryjek and Vera (1986) proposed a modification of the PR EOS in which the temperature-dependent function $\alpha[T_R]$ was modified to extend the range of applicability to polar components as follows:

$$\alpha[T_R] = \left\{1 + m[1 - T_R{}^{0.5}]\right\}^2 \tag{2.15}$$

$$\begin{aligned} m = {} & (0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3) \\ & + \kappa_1\left(1 + \left(\frac{T}{T_c}\right)^{0.5}\right)\left(0.7 - \left(\frac{T}{T_c}\right)\right) \end{aligned} \tag{2.16}$$

where $\kappa_1$ is an adjustable parameter characteristic of each pure component. Some other expressions of the temperature-dependent function $\alpha[T_R]$ in the attractive term of the SRK and PR EOS have been proposed by Gibbons and Laughton (1984), Ishikawa et al.

(1980), Mathias (1983), Mathias and Copeman (1983), Melhem et al. (1989), Nasrifar and Moshfeghian (2001), Soave (1979), and Twu et al. (1995a; 1995b).

Patel and Teja (PT: Patel and Teja 1982) proposed an equation of state that improves saturation property predictions, especially for heavy hydrocarbon and polar substances, while maintaining the good features of PR and SRK equations. The PT EOS has the following form:

$$P = \frac{RT}{v-b} - \frac{a[T]}{v(v+b)+c(v-b)} \tag{2.17}$$

where

$$a[T] = \Omega_a \frac{R^2 T_c^2}{P_c} \alpha[T_R] \tag{2.18}$$

$$b = \Omega_b \frac{RT_c}{P_c} \tag{2.19}$$

$$c = \Omega_c \frac{RT_c}{P_c} \tag{2.20}$$

$$\Omega_c = 1 - 3\zeta_c \tag{2.21}$$

$$\Omega_a = 3\zeta_c^2 + 3(1-2\zeta_c)\Omega_b + \Omega_b^2 + 1 - 3\zeta_c \tag{2.22}$$

and $\Omega_b$ is the smallest positive root of the following equation

$$\Omega_b^3 + (2-3\zeta_c)\Omega_b^2 + 3\zeta_c^2\Omega_b - \zeta_c^3 = 0 \tag{2.23}$$

$$\alpha = [1 + F(1 - T_R^{1/2})]^2 \tag{2.24}$$

where

$$\zeta_c = \frac{P_c V_c}{R T_c} \tag{2.25}$$

The critical compressibility factor $\zeta_c$ is not necessarily equal to the value from experiments, but is treated as an empirical parameter. The optimum value of $\zeta_c$ and $F$ are obtained by minimizing deviations between saturated liquid densities and vapor pressures calculated from PT EOS and experimental values. For nonpolar substances:

$$\zeta_c = 0.329032 - 0.076799\,\omega + 0.0211947\,\omega^2 \tag{2.26}$$

$$F = 0.452413 + 1.30982\,\omega - 0.295937\,\omega^2 \tag{2.27}$$

The cubic equations of state presented above are all based on the vdW EOS with the modifications of the vdW "attractive" intermolecular interaction term. However, at moderate to high densities, repulsive interactions can be expected to be the dominant influence in determining fluid properties. Several modified "repulsive" terms of vdW EOS have therefore been developed.

The most widely used modified hard-sphere term is the equation proposed by Carnahan and Staring (1969). The Carnahan-Staring-van der Waals (CSvdW) equation is formed by coupling this hard-sphere repulsion term with the van der Waals attractive term (Carnahan and Starling 1972):

$$P = \frac{RT(1+\eta+\eta^2-\eta^3)}{v(1-\eta)^3} - \frac{a}{v^2} \tag{2.28}$$

where $\eta$ is the packing fraction defined in terms of the molecular covolume (*b*):

$$\eta = \frac{b}{4v} \tag{2.29}$$

Sadus (1993) has demonstrated that the CSvdW EOS can be used to predict type III phase behavior with considerable accuracy. Other hard sphere expressions can be found in Guggenheim (1965), Scott (1971) , Boublik (1981), Kolafa and Nezbeda (1994), and Malijevsky and Veverka (1999).

The equations of state presented above are just some of the hundreds of equations of state that have been published, and reviewed in Sandler (1994), Sengers et al.(2000), and Wei and Sadus (2000).

### 2.3.2 Mixing Rules

In order to extend an equation of state to mixtures, the characteristic constants *a*, *b*, and *c* must be obtained using mixing rules.

The van der Waals 'one fluid' mixing rules are the most popular and widely used mixing rules, and are given by:

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{2.30}$$

$$b = \sum_i x_i b_i \tag{2.31}$$

$$c = \sum_i x_i c_i \tag{2.32}$$

The term $a_{ij}$ represents a measure of the strength of attraction between a molecule $i$ and a molecule $j$. For $i \neq j$ , this cross-term $a_{ij}$ is typically calculated with the following combining rule:

$$a_{ij} = \sqrt{a_i a_j}\,(1 - k_{ij}) \tag{2.33}$$

where $k_{ij}$ is the binary interaction parameter that is taken as an adjustable parameter to correlate data.

In general, the simple van der Waals mixing rules in equation (2.30) to (2.32) can reasonably represent behavior of normal fluids, often without any binary interaction parameters. However, modifications of the mixing rules are usually needed if the fluids are polar or highly non-ideal. Panagiotopoulos and Reid (1986) introduced an asymmetric $(k_{ij} \neq k_{ji})$ combining rule for the cross term $a_{ij}$ as follows:

$$a_{ij} = \sqrt{a_i a_j}\left(1 - k_{ij} + (k_{ij} - k_{ji})x_i\right) \tag{2.34}$$

This mixing rule allows the equations of state to be adjusted at different compositions. Other mixing rules that use a compositions-dependent binary interaction parameter can

also be found. (Adachi and Sugie 1986; Panagiotopoulos and Reid 1986; Schwartzentruber and Renon 1989; Stryjek and Vera 1986). However, many of these mixing rules suffer from 'the problem of invariance' discussed by Michelsen and Kistenmacher (1990). One of the modifications of quadratic mixing rules and solved the invariance problem was proposed by Mathias et al(1991), called Mathias-Klotz-Prausnitz (MKP) mixing rule as shown below:

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j}\left(1 - k_{ij}\right) + \sum_i x_i \left( \sum_j x_j \left(\sqrt{a_i a_j}\right)^{1/3} l_{ji}^{1/3} \right)^3 \qquad (2.35)$$

where $k_{ij}$ ($=k_{ji}$) is a symmetric binary parameter, and $l_{ij}$ and $l_{ji}$ are antisymmetric ($l_{ij} = -l_{ji}$). In many cases, the MKP mixing rule provides good representations of the phase equilibria of highly non-ideal mixtures and systems containing two similar components and the third is different such as water in hydrocarbon mixture (Mathias et al. 1991; Pfohl et al. 1997; Pfohl et al. 1999).

Other approachs to mixing rules modifications are based on excess Gibbs energy models. Huron and Vidal (1979) successfully formulated the constant $a$ of equations of state by assuming that the excess Gibbs energy at infinite pressure $G_\infty^E$, which is derived from an equation of state, is equal to the excess Gibbs energy derived from a liquid activity coefficient model. It was also assumed that the liquid volume at infinite pressure equals the covolume parameter $b$. The Huron-Vidal derivation led to the following equations:

$$a^* = b^* \left[ \sum_i x_i \frac{a_i^*}{b_i^*} + \frac{1}{C_1} \left( \frac{G_\infty^E}{RT} \right) \right] \tag{2.36}$$

where

$$a^* = Pa / R^2 T^2 \tag{2.37}$$

$$b^* = Pb / RT \tag{2.38}$$

$$C_1 = -\frac{1}{(w-u)} \ln \left( \frac{1+w}{1+u} \right) \tag{2.39}$$

where $u$ and $w$ are equation of state dependent constants used to represent a particular two-parameter cubic equation of state (Twu et al. 2002a).

From this pioneering work of Huron and Vidal (1979), a number of publications proposed new ways to combine excess Gibbs energy models with equations of state. Examples can be found in the work of Heidemann and Kokal (1990), Dahl and Michelsen (1990), Wong and Sandler (1992), Soave (1992), Twu and Coon (1996), Abovsky and Watanasiri (1999), and Twu et al. (2002b). The Wong and Sandler mixing rule (1992) has the following form:

$$\frac{a_m}{b_m} = \sum \left\{ x_i \frac{a_i}{b_i} + \frac{A_\infty^E}{C} \right\} \tag{2.40}$$

$$b_m = \frac{\sum\sum x_i x_j \left\{ b - \frac{a}{RT} \right\}_{ij}}{1 - \frac{A_\infty^E}{CRT} - \sum x_i \left( \frac{a_i}{b_i RT} \right)} \tag{2.41}$$

$$\left( b - \frac{a}{RT} \right)_{ij} = \frac{1}{2} \left\{ \left( b_i - \frac{a_i}{RT} \right) + \left( b_j - \frac{a_j}{RT} \right) \right\} (1 - k_{ij}) \tag{2.42}$$

where $a_m$ and $b_m$ are mixture parameters, C is a constant dependent on the equation of state, $A_\infty^E$ is the excess Helmholtz energy at infinite pressure obtained from activity coefficient models, and $k_{ij}$ is an adjustable parameter. Wong et al. (1992) showed that the Wong-Sandler (1992) mixing rules can be used for highly non-ideal mixtures. Furthermore, the main attraction of the Wong-Sandler mixing rule follows from its ability to extrapolate vapor-liquid equilibrium data to higher temperatures and pressures. Some of the reviews and comparisons of several mixing rules can be found in the works of Knudsen et al.(1993), Smith and Teja (1995), Orbey and Sandler (1996), Wei and Sadus (2000), Valderrama (2003).

# CHAPTER 3

# EXPERIMENTAL

This chapter describes the experimental apparatus and procedure, and presents the experimental results obtained in this study. The synthetic method was employed for phase equilibrium measurements. Each point on the phase envelope was obtained by observation of new phase formation at constant temperature.

## 3.1 Phase Equilibrium Measurements

### 3.1.1 Experimental Apparatus

A schematic diagram of the apparatus used in this work is shown in Figure 3.1. A commercial Phase Equilibrium Analyzer (PEA) consisting of a variable-volume equilibrium vessel, a high-pressure syringe pump, and software were purchased from Thar Technologies, Inc. (Pittsburgh, PA) and used to measure phase equilibria.

The variable-volume equilibrium vessel consisted of a high pressure vessel (70 mm o.d., 20 mm i.d.) fitted with a 12.65 mm thick sapphire window and a movable plunger with a magnetic stirrer. The vessel was rated to 380 bar at 393 K and its volume could be adjusted from 6.00 ml to 30.00 ml by controlling of the movement of a plunger using the PEA software. The water jacket of the vessel was connected to a constant temperature circulator (VWR Scientific Products, model 1157), which could be set from 243 K to 473 K within ± 0.01 K. The temperature inside the equilibrium vessel was measured with a four-wire class A RTD probe (Conax, Buffalo NY) connected to a

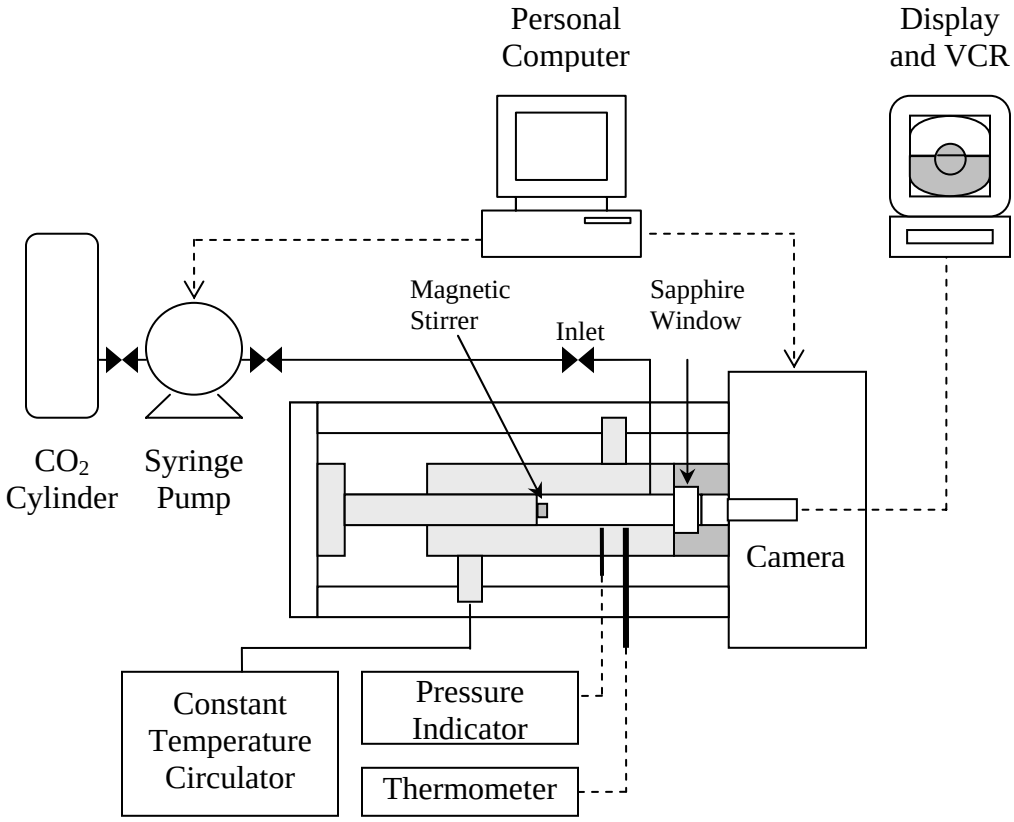


**Figure 3.1:** Experimental Apparatus

digital thermometer (Model 7563, Yokogawa, Newnan GA). The RTD probe and the thermometer were calibrated against a calibrated digital thermometer with a platinum probe (Fluke, model 2180A) as shown in Appendix A. The accuracy of the thermometer was 0.01%.

The pressure inside the vessel was measured with a pressure transducer (Model S, Sensotec, Columbus OH) and an indicator (Sensotec, Model SC100). The pressure transducer was factory calibrated and certified to ±0.5% accuracy at full scale. The contents inside the vessel were projected onto a monitor using a built-in video camera.

The high-pressure syringe pump (Thar Technologies, Inc.) was connected to a cooling water system (GCA/Precision Scientific, model 254) to liquefy and store carbon dioxide from a cylinder. The pressure in the syringe pump was controlled with PEA software by adjusting the internal volume of the pump at constant temperature.

### 3.1.2 Materials

Coleman grade carbon dioxide (99.99% purity) was purchased from Airgas (Radnor, PA) and was used as received. Pyrrole (99% purity) was purchased from ACROS Organic (Somerville, NJ), and was refrigerated prior to use. 1-Butanol (used for experimental procedure validation) was purchased from Fisher Scientific (Fair Lawn, NJ) with a stated purity of 99.5%.

### 3.1.3 Experimental Procedure

Before starting the experiment, the empty vessel was purged several times with low pressure carbon dioxide. A liquid sample of one of the components was then transferred to the equilibrium vessel using a syringe. The mass of sample loaded was determined from the difference between the weight of a syringe before and after loading,

with the sample. The syringe was weighed on a digital balance (Model 1872MP8, Sartorius, Westbury NY) with an accuracy of ± 0.1 mg. The inlet valve of the vessel was temporarily disconnected in order to inject the sample. It was assumed that the amount of air entering the vessel during sample loading was negligible.

After the inlet valve was reconnected, carbon dioxide was introduced into the vessel from the syringe pump. The amount of carbon dioxide was determined from the volume displacement of the pump and the density of carbon dioxide at the pump pressure and temperature calculated using the equation of state of Span and Wagner (1996).

The binary mixture of pyrrole and carbon dioxide in the vessel was then compressed by moving the plunger until a homogeneous mixture was obtained. The vessel contents were left for at least 30 minutes with stirring to obtain thermal equilibrium at the temperature of interest. The phase equilibrium pressure was initially estimated by increasing the volume of the vessel until the formation of a new phase was visually observed. The actual pressure was subsequently determined using the procedure discussed below.

The mixture was recompressed until a homogeneous phase was again observed. The vessel volume was then increased in a stepwise manner while the temperature was maintained at the desired value within ± 0.2 K. The gauge pressure after each step of 0.01 ml change of vessel volume was recorded. The gauge pressure read from the transducer plus the atmospheric pressure correction were then plotted against the volume of the vessel during depressurization at constant temperature.

Figure 3.2 shows typical results of the depressurization of a carbon dioxide + pyrrole mixture at 313 K (0.465 mole fraction pyrrole). The pressure – volume line

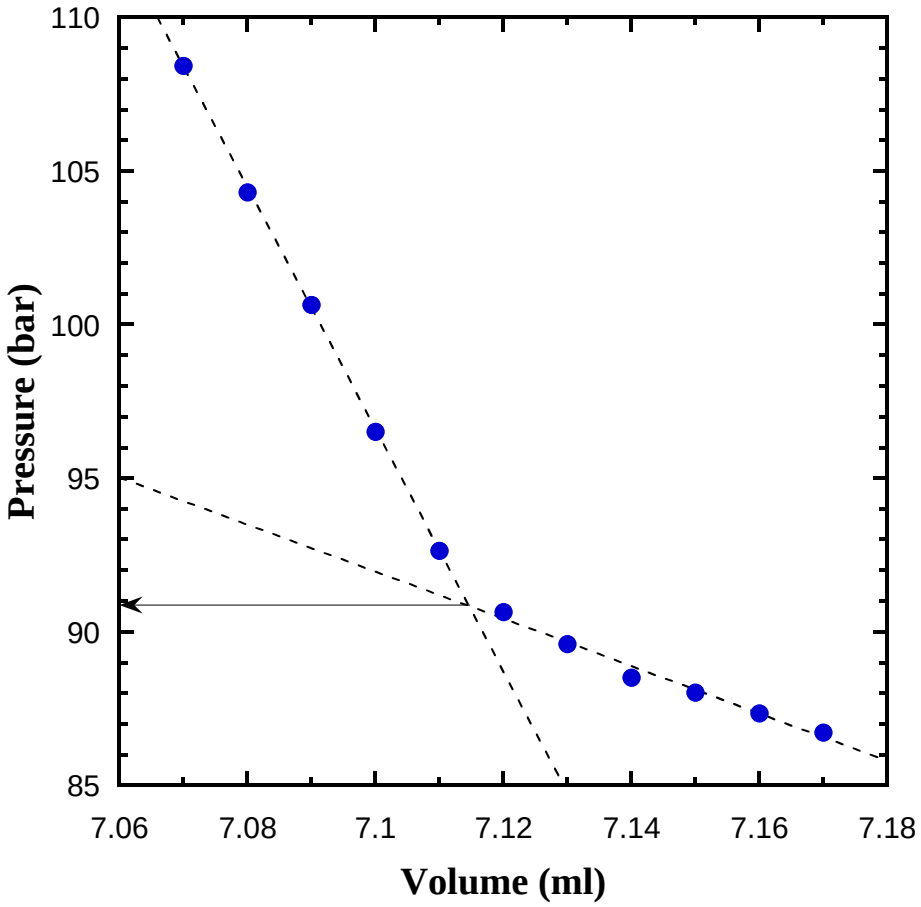


**Figure 3.2:** Pressure – Volume Relation for the Depressurization of Carbon Dioxide (1) + Pyrrole (2) at T = 313 K, $x_2$ = 0.465

changes slope as shown when a new phase with a different isothermal compressibility appears. The intersection of the two lines yields the phase equilibrium pressure. For a given loading of the vessel, the phase equilibrium pressure measurements were reproduced at least twice to within ± 0.3 bar and ± 0.2 K.

### 3.1.4 Experimental Error

A possible experimental error involves the determination of carbon dioxide composition in the mixture. One source of this error was temperature fluctuation in the pump during carbon dioxide loading. This could have resulted in as much as 1% error in the calculation of the amount of carbon dioxide. Another source of error was the carbon dioxide present in the vessel after purging but before carbon dioxide loading. This accounted for no more than 0.6% of the carbon dioxide in the mixture. The mole fractions are estimated to be accurate within ± 0.001 after taking all these sources of error into account.

## 3.2 Validation of Experimental Technique

In order to validate the experimental technique, the system carbon dioxide + 1-butanol was investigated at 313 K and the data obtained were compared with literature data. LV type of phase behavior was observed (bubble points) for the entire range of mixture compositions studied in this work as presented in Table 3.1. Data of this work along with the data of Byun (2002) at 313 K and Jennings (1991) at 314.8 K are plotted in Figure 3.3. Byun used a synthetic method that was similar to that used in this work, while Jennings used a flow method to obtain his data. Note that the new data show good agreement (average 1% difference in pressure) with the data of both investigators.

**Table 3.1:** Phase Equilibrium Data for Carbon Dioxide + 1-Butanol at 313 K

| **Mole fraction of 1 - butanol** | **Pressure (bar)** | **Type of phase behavior** |
|---|---|---|
| 0.164 | 83.1 | LV |
| 0.211 | 82.5 | LV |
| 0.255 | 81.3 | LV |
| 0.349 | 79.3 | LV |
| 0.402 | 77.6 | LV |
| 0.456 | 74.8 | LV |
| 0.494 | 69.6 | LV |

LV: Liquid-vapor

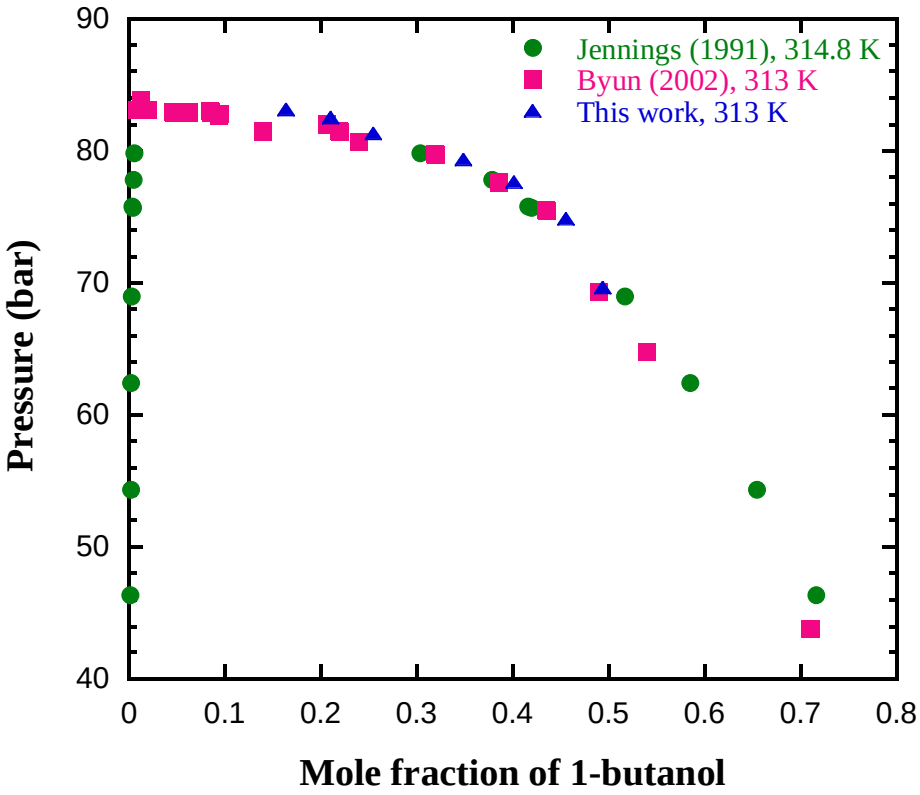


**Figure 3.3**: Phase Equilibria in the Carbon Dioxide + 1- Butanol System

### 3.3 Experimental Results and Discussion

Phase equilibria in the carbon dioxide + pyrrole system were measured at 313 K, 323 K, and 333 K. The results are presented in Table 3.2 to Table 3.4 and illustrated in Figure 3.4. Details are given below.

At 313 K, liquid – liquid immiscibility or LL type of phase behavior was observed at pyrrole mole fractions of 0.11 to 0.355. The appearance of the second liquid phase could be detected visually as a result of cloud formation in the vessel. At the end of the depressurization process, two liquid layers could be seen. At the pyrrole mole fractions of 0.11, 0.138, and 0.233, the second liquid phase formed was the heavier phase rich in pyrrole. On the other way, the second liquid phase formed was the lighter phase rich in carbon dioxide at the pyrrole mole fractions of 0.233, 0.305, and 0.355.

At 313 K and pyrrole mole fractions 0.416, 0.465, and 0.533, LV or bubble point behavior was observed where a small vapor bubble appeared in the vessel as the pressure was lowered.

At 313 K and pyrrole mole fraction of 0.07, LV or dew point behavior was observed, where a small amount of liquid formed in the vessel as the pressure was lowered. Dew points were difficult to detect visually with this type of experimental set up (horizontal vessel). The reason is that the first drop of liquid may appear as a thin film on the wall, rather than as a drop at the bottom of the vessel, and could easily be overlooked.

At 323 K, LL type of phase behavior was detected at pyrrole mole fractions of 0.233, 0.305, and 0.355, whereas LV phase behavior (bubble points) was detected at

**Table 3.2:** Phase Equilibrium Data for Carbon Dioxide + Pyrrole at 313 K

| **Mole fraction of pyrrole** | **Pressure (bar)** | **Type of phase behavior** |
|---|---|---|
| 0.070 | 86.3 | LV |
| 0.110 | 97.8 | LL |
| 0.138 | 100.2 | LL |
| 0.180 | 105.8 | LL |
| 0.233 | 107.6 | LL |
| 0.305 | 108.8 | LL |
| 0.355 | 101.6 | LL |
| 0.416 | 93.3 | LV |
| 0.465 | 90.8 | LV |
| 0.533 | 84.0 | LV |

LV: Liquid-vapor. LL: Liquid-liquid

**Table 3.3:** Phase Equilibrium Data for Carbon Dioxide + Pyrrole at 323 K

| Mole fraction of pyrrole | Pressure (bar) | Type of phase behavior |
|---|---|---|
| 0.233 | 131.3 | LL |
| 0.305 | 132.4 | LL |
| 0.355 | 126.7 | LL |
| 0.465 | 116.8 | LV |

**Table 3.4:** Phase Equilibrium Data for Carbon Dioxide + Pyrrole at 333 K

| Mole fraction of pyrrole | Pressure (bar) | Type of phase behavior |
|---|---|---|
| 0.233 | 151.4 | - * |
| 0.305 | 151.5 | - * |
| 0.355 | 146.3 | LL |

* Could not be determined from visual observation

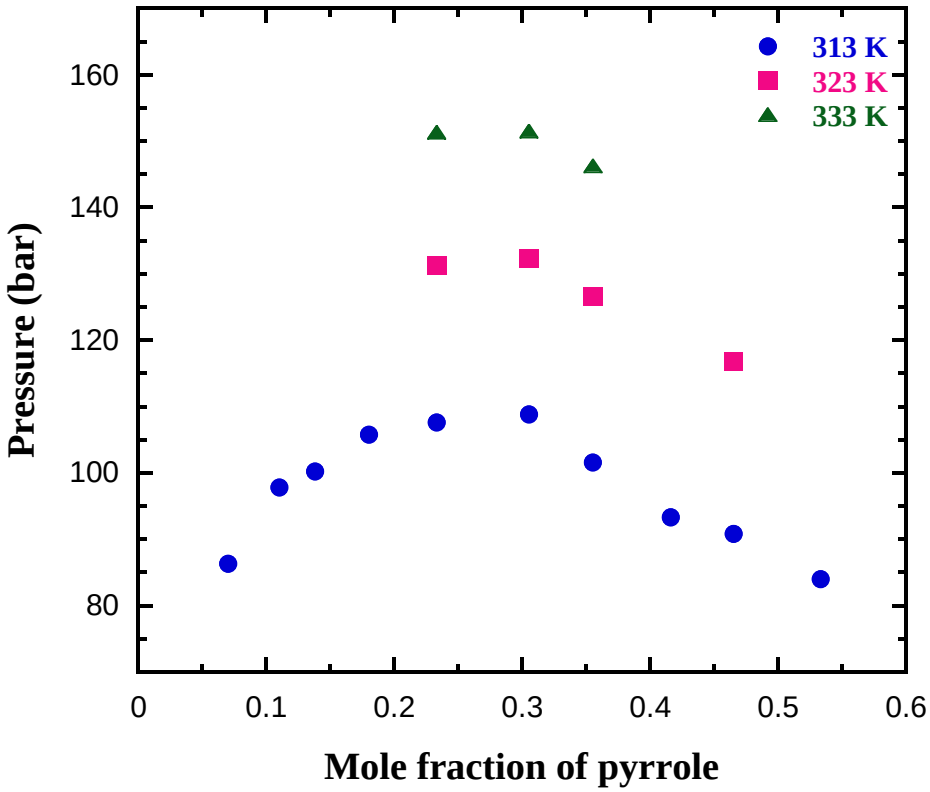


**Figure 3.4**: Phase Equilibria in the Carbon Dioxide + Pyrrole System

pyrrole mole fractions of 0.465. For measurements at 333 K, LL type of phase behavior could be detected visually only at a pyrrole mole fraction 0.355. At pyrrole mole fractions of 0.233 and 0.305, visual observations were not sufficient to determine whether the phase transition that occurred was of LL or LV type because of the dark color of the mixture in the equilibrium vessel.

# CHAPTER 4

# THERMODYNAMIC MODELING

This chapter presents the correlation of the phase equilibrium results from the previous chapter. The predicted type of phase behavior of carbon dioxide + pyrrole system is also presented.

## 4.1 Thermodynamic Model

A cubic equation of state was chosen to correlate the experimental results due to the simplicity of the model and the fact that the model could be easily extended to multicomponent systems. Cubic equations such as PR, SRK, and PT have been widely applied to phase equilibria of mixtures containing SCF. In this work, the PT equation was chosen to correlate data in the carbon dioxide + pyrrole system since the PT EOS is superior to the SRK and PR EOS when applied to polar substances.

The mixing rule chosen was the MKP mixing rule with two adjustable parameters. It offers a particularly simple way to represent polar mixtures and non-ideality better than the simple van der Waals mixing rules.

## 4.2 Validation of the Model

The thermodynamic model used in this work (PT EOS + MKP mixing rule) was validated with data for carbon dioxide + 1-hexanol at 303.15 K, because this system exhibits liquid-liquid phase behavior at high pressure as reported by Beier et al. (2003) , Chylinski and Gregorowicz (1998) , and Lam et al. (1990).

The carbon dioxide – 1-hexanol data from Beier et al. (2003) were correlated with PT EOS + MKP mixing rule. The area method was employed as a phase equilibrium

calculation algorithm, and is discussed in Appendix B. Figure 4.1 shows the results with the best fit of the data corresponding to $k_{12}$ = 0.097 and $l_{12}$ = 0.032 evaluated by trial-and-error. A good fit of the LV region, but only a qualitative fit of the LL envelope was obtained.

Beier et al. (2003) used the Soave-Redlich-Kwong equation (Soave 1972a) and Huron and Vidal (1979) mixing rule to correlate their data. They obtained a good fit of the bubble-points and a somewhat better fit of the liquid-liquid envelope at 303.15 K. Their calculated LL critical point was ~15 bar above the experimental value. However, they did use three adjustable parameters in their work. Similarly to the PT EOS + MKP mixing rule, the SRK EOS + HV mixing rule qualitatively predicts the phase equilibrium with LL behavior at high pressure.

**4.3 Phase Equilibrium Calculation for the Carbon Dioxide + Pyrrole System**

Phase equilibrium data for carbon dioxide + pyrrole obtained in this work at 313 K, 323 K, and 333 K were correlated using the PT EOS with the MKP mixing rule and two binary interaction parameters $k_{12}$ and $l_{12}$ evaluated by trial-and-error. The values $k_{12}$ = 0.086 and $l_{12}$ = 0.045 provided the best representation of experimental data at 313 K. These values of binary interaction parameters were also used in calculations for all isotherms. Critical properties and acentric factors of the two components were obtained from DIPPR (2003).

The results of the correlations are shown along with the experimental data in Figure 4.2. At 313 K, the calculated phase behavior shows a liquid-liquid phase envelope

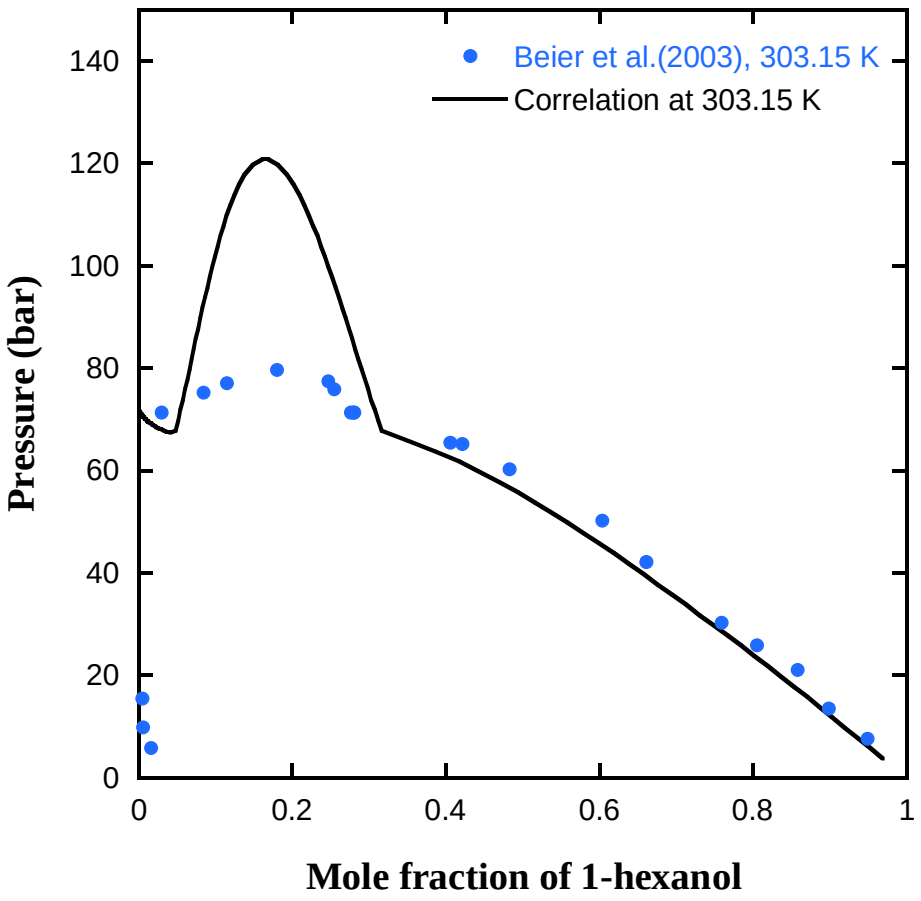


**Figure 4.1**: Experimental Data (Beier et al. 2003) and Calculated Phase Equilibrium Behavior for Carbon Dioxide + 1-Hexanol with PT EOS + MKP Mixing Rule ( $k_{12}$ =0.097, $l_{12}$ =0.032)

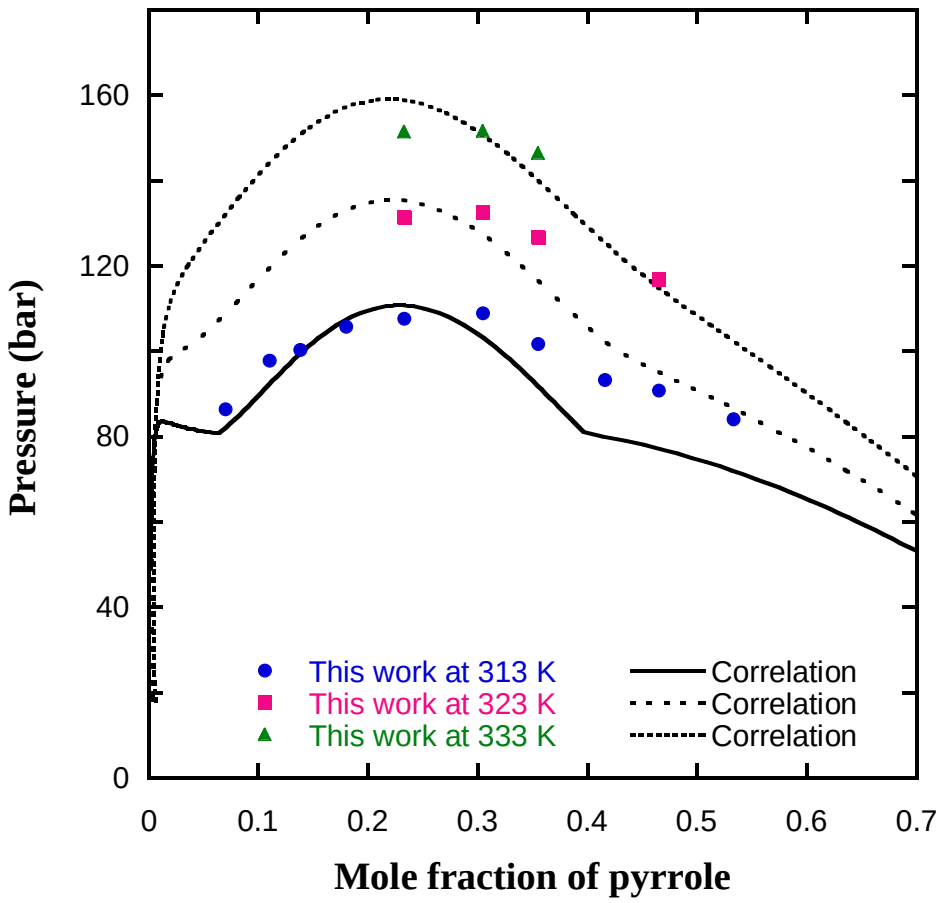


**Figure 4.2**: Experimental Data and Calculated Phase Equilibrium Behavior for Carbon Dioxide + Pyrrole with PT EOS + MKP Mixing Rule ($k_{12}$ =0.086, $l_{12}$ =0.045)

and a small vapor-liquid phase envelope. A reasonable fit of the data is obtained over the liquid-liquid composition range, although the fit of bubble-point and dew-point curves is poorer.

At 323 K and 333 K, only liquid – liquid behavior was detected. Note that even though the binary interaction parameters used were evaluated from the data at 313 K, the PT EOS was able to represent the phase behavior of the carbon dioxide + pyrrole system at 323 and 333 K quite well.

**4.4 Pressure – Temperature Diagram for the Carbon Dioxide + Pyrrole System**

In order to determine the type of phase behavior of the carbon dioxide + pyrrole system, calculated critical points were plotted using the PT EOS + MKP mixing rule with $k_{12}$ and $l_{12}$ determined at 313 K ($k_{12}$ = 0.086, $l_{12}$ = 0.045). The results are shown in Figure 4.3. The solid line in the figure represents the vapor pressure of pure carbon dioxide (DIPPR 2003) and ends at its critical point ($T_c$ = 304.21 K, $P_c$ = 73.83 bar). Solid circles represent calculated critical points from LL or LV phase envelopes (maximum pressures of the pressure-composition diagram), and the solid triangles show LLV phase behavior. The dashed lines represent extrapolations of the critical behavior in this system.

The lines suggest that the phase behavior of the carbon dioxide + pyrrole system is of type IV in the classification of Scott and van Konynenburg (1970). This type is characterized by a steep UCST line at low temperatures, and an LLV region located very close to the critical point of the more volatile component.

The carbon dioxide + pyrrole system is thus one of the very few carbon dioxide binary mixtures showing type IV fluid phase behavior. Similar behavior can be found in carbon dioxide + nitrobenzene (Kohnstamm and Reeders 1913), + o-nitrophenol

(Scheffer and Smittenberg 1933), + *n*-tridecane (Fall and Luks 1985), and + 1-pentanol (Raeissi et al. 1998).

The phase behavior of carbon dioxide + pyrrole can be used to infer phase behavior in the carbon dioxide + polypyrrole. Figure 4.4B shows the phase behavior of solvent-polymer systems that is similar to type IV behavior (Figure 4.4A) in solvent + small molecule systems (Kirby and McHugh 1999). From Figure 4.4B, it can be seen that the large difference in size between solvent + polymer in the mixture suppresses several features of the phase diagram in the solvent + small molecule system. At high temperatures, the LCST curve does not reach a distinct end point because polymers do not have critical points. Also, the LLV lines for a solvent + polymer mixture superimpose onto the vapor pressure curve of the solvent. Note that both UCST and LCST branches of the critical mixture curves are often referred to as 'cloud point curves', and the locations of these cloud points curves depend on the type and molecular weight of the polymer for a specific solvent. Since the the carbon dioxide + pyrrole system exhibits type IV phase behavior, it can be suggested that the P-T diagram of the carbon dioxide + polypyrrole could be that shown in Figure 4.4B.

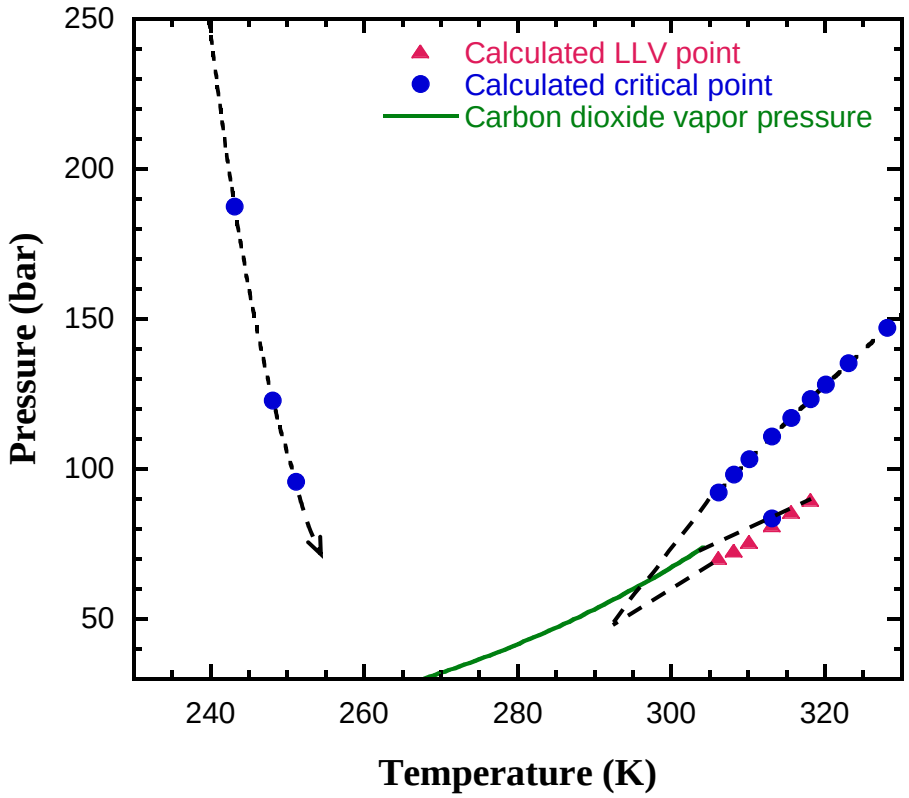


**Figure 4.3**: Calculated Pressure-Temperature Projection for Carbon Dioxide + Pyrrole with PT EOS + MKP Mixing Rule ($k_{12}$=0.086, $l_{12}$=0.045). The Dashed Lines Represent Possible Extrapolations.

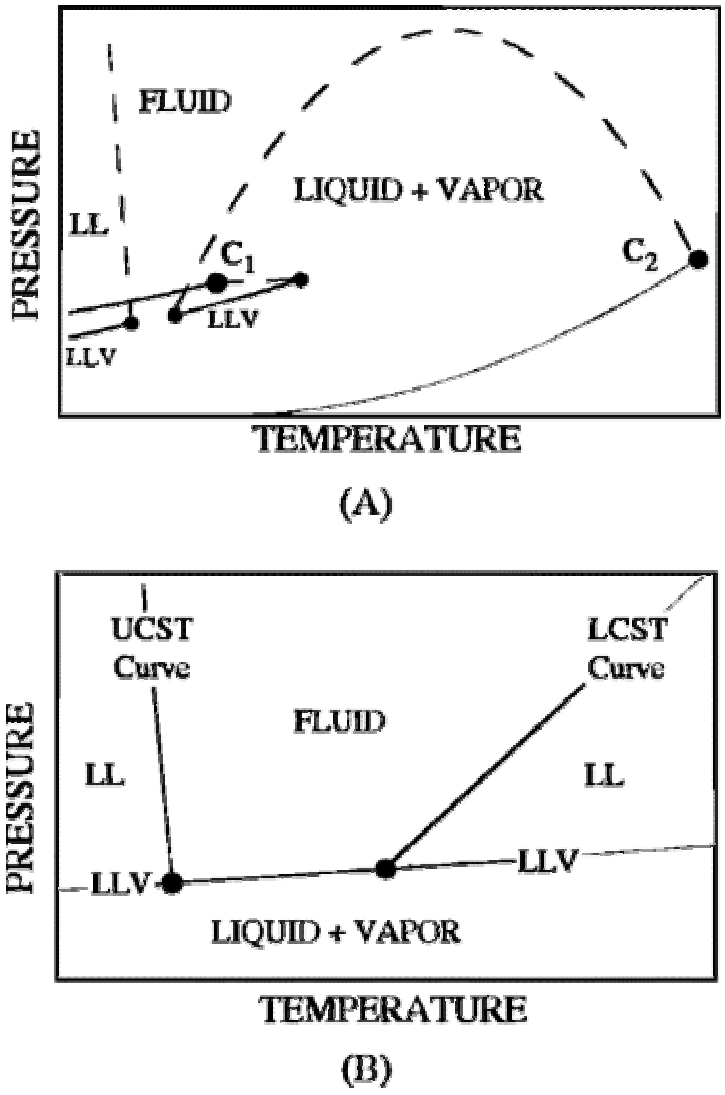


**Figure 4.4**: Pressure-Temperature Diagrams for Binary Mixtures of Low Molecular Weight Solvent with (A) a Low Molecular Weight Solute (B) a High Molecular Weight Polymer.

# CHAPTER 5

# CONCLUSIONS AND RECOMMENDATIONS

## 5.1 Conclusions

High pressure phase equilibria in the carbon dioxide + pyrrole system were measured at different temperatures using a synthetic method. The measurements were performed at 313 K, 323 K, and 333 K which are temperatures of interest for supercritical processing. The results showed that the LL phase behavior was observed at 313 K at the pyrrole mole fractions from 0.11 to 0.355. Similarly, LL phase behavior was also observed at 323 K and 333 K.

In this study, the Patel-Teja equation of state + Mathias-Klotsz-Prausnitz mixing rule was employed in correlating and predicting phase behavior. The fit of the model with the carbon dioxide + 1-hexanol data at 303.15 K from Beier (2003) demonstrates the limitation of the cubic equations of state to accurately correlate LL data. Nevertheless, it shows that the PT EOS is able to predict the presence of LL phase behavior at high pressure using only two adjustable parameters.

For the carbon dioxide + pyrrole system, the PT EOS + MKP mixing rule provided a qualitative fit of the experimental data at 313 K. Additionally, a small LV phase envelope was predicted at low pyrrole mole fractions. The two binary interaction parameters in the model were obtained from this fit at 313 K and were used to calculate the remaining isotherms (323 K and 333 K). These isotherms show reasonable agreement with the experimental data.

The pressure – temperature diagram of the carbon dioxide + pyrrole system was obtained from the calculated phase behavior at 313 K, 323 K, 333 K and additional predicted isotherms. The results suggest that this binary system exhibits type IV phase behavior as classified by Scott and van Konynenburg (1970), which, furthermore, can be inferred to the type of phase behavior for carbon dioxide + polypyrrole. Future research can, therefore, take advantage of the predicted phase behavior from this work in the development of novel processes and in improving current processes that involve carbon dioxide + pyrrole system.

**5.2 Recommendations**

The synthetic method used in this work provides reliable measurements of phase behavior, especially near the critical points. However, the accuracy of the data can be increased by improving mixture preparations procedures and temperature control. During carbon dioxide loading, fluctuations in temperature and pressure in the syringe pump can cause errors in determining the mass of carbon dioxide added leading to errors in mixture composition. Carbon dioxide should therefore be transfer via a high-pressure bomb (McHugh and Krukonis 1994) and its mass should be determined.

In this work the temperature of the equilibrium vessel was controlled by a constant temperature circulator, which could only be adjusted manually. Thus, it was difficult to maintain a constant temperature during the pressurization – depressurization process. Therefore, it is suggested that a controller be added to maintain the temperature of the equilibrium vessel.

In addition to the experimental data obtained in this work, it would be interesting to study the phase behavior of carbon dioxide + pyrrole further at low pyrrole mole

fraction at 313 K, since the correlation result shows a small liquid-vapor phase envelope at this region. However, it is suggested that the analytical method be used for dew point measurements at low mole fractions of pyrrole. This is because the synthetic method may leads to large error from determination of very small amount of pyrrole weighed into the equilibrium cell, and due to the overlooking of dew points.

In addition to the study of phase behavior of carbon dioxide + pyrrole system, it would also be interesting to study the binary phase behavior of carbon dioxide with thiophene, and furan. These two components are similar to pyrrole in that they are aromatic five-membered heterocycles and have been used as monomers for the preparation of electrically conducting polymers (Abbett et al. 2003a; Tsurumaki and Tasaka 1995). It would be interesting to see if the systems also exhibit type IV phase behavior.

## APPENDIX A

## TEMPERATURE CALIBRATION

A Yokogawa model 7563 digital thermometer with a four-wire class A RTD probe (Conax Buffalo Technologies) was used to measure temperature inside the vessel. This was calibrated against a calibrated digital thermometer with a Fluke model 2180A platinum probe. Both probes were placed in a constant temperature water bath and the temperatures were recorded (Table A.1). The average residual of the thermocouples was 0.07 ºC.

**Table A.1:** Temperature Calibration of Digital Thermometer + RTD Probe

| **Temperature (Fluke) (ºC)** | **Temperature (Yokogawa) (ºC)** | **Residuals ($T_{Fluke} - T_{Yokogawa}$)** |
|---|---|---|
| 29.86 | 29.78 | 0.08 |
| 34.84 | 34.78 | 0.06 |
| 39.88 | 39.81 | 0.07 |
| 44.91 | 44.84 | 0.07 |
| 49.92 | 49.85 | 0.07 |

## APPENDIX B

## THE AREA METHOD

The area method is a phase equilibrium algorithm proposed by Eubank (1992). This method is based on integrating the Gibbs energy of mixing curve. For a binary mixture at a specified temperature and pressure, the Gibbs energy of mixing can be calculated from:

$$\frac{\Delta G_m}{RT} = x_1 \ln x_1 + x_2 \ln x_2 + \frac{1}{RT}\int_0^P v dP - \frac{x_1}{RT}\int_0^P v_1 dP - \frac{x_2}{RT}\int_0^P v_2 dP \qquad \text{(B.1)}$$

where $v$ is the molar volume of phase, and $v_1$ and $v_2$ are the molar volumes of pure components 1 and 2, respectively. The integration terms in equation (B.1) can be calculated from an equation of state with an appropriate mixing rule using a numerical integration technique, such as the Trapezoidal Rule (Chapra and Canale 1998).

The objective of the area method is to find the maximum area which can be expressed mathematically (when $\Delta G_m / RT \equiv \phi$) as:

$$\mathrm{A}\left(x^a, x^b\right) = \left| \left(\phi\left(x^b\right) + \phi\left(x^a\right)\right)\frac{\left(x^b - x^a\right)}{2} \right| - \left| \int_{x^a}^{x^b} \phi(x) dx \right| \qquad \text{(B.2)}$$

where at equilibrium $$\mathrm{A}\left(x^I, x^{II}\right) = \max \mathrm{A}\left(x^a, x^b\right) \qquad \text{(B.3)}$$

As shown in Figure B.1, the area $A(x^a, x^b)$ from the equation (B.2) can be explained as the net area between a trapezoid, formed by two points $(x^a, x^b)$ on the composition axis, and the area of the Gibbs energy of mixing curve integrated between $(x^a, x^b)$ . The two compositions represent the equilibrium composition $(x^I, x^{II})$ only if the area $A(x^a, x^b)$ is at its maximum and positive value, as shown in Figure 4.1 by the shaded area. If the area is negative in the entire composition range, there exists only a single phase. For the second largest value of the area calculated from equation (B.1), a pair of compositions will be an equilibrium pair $(x^{III}, x^{IV})$ only if the range $(x^{III}, x^{IV})$ is outside that of $(x^I, x^{II})$ .

The area method has a major advantage that it does not need an initial guess in the calculations. This also means that it does not leave any possible phase split uninvestigated. The area method has been used successfully in several phase equilibrium calculations especially in the near-critical region (Firouzi et al. 1998; Fotouh and Shukla 1996; Hodges et al. 1995; Sun and Teja 1998).

As an example, the plots of Gibbs energy of mixing – pyrrole mole fraction at a temperature of 313 K and pressure of 82 bar were shown in Figure B.2 and B.3. Two two-phase regions are observed, which correspond to liquid-vapor and liquid-liquid equilibrium. The phase equilibrium compositions calculated are at pyrrole mole fraction of 0.0075 and 0.0345 for liquid-vapor phase behavior, and 0.0701 and 0.3928 for liquid-liquid phase behavior.

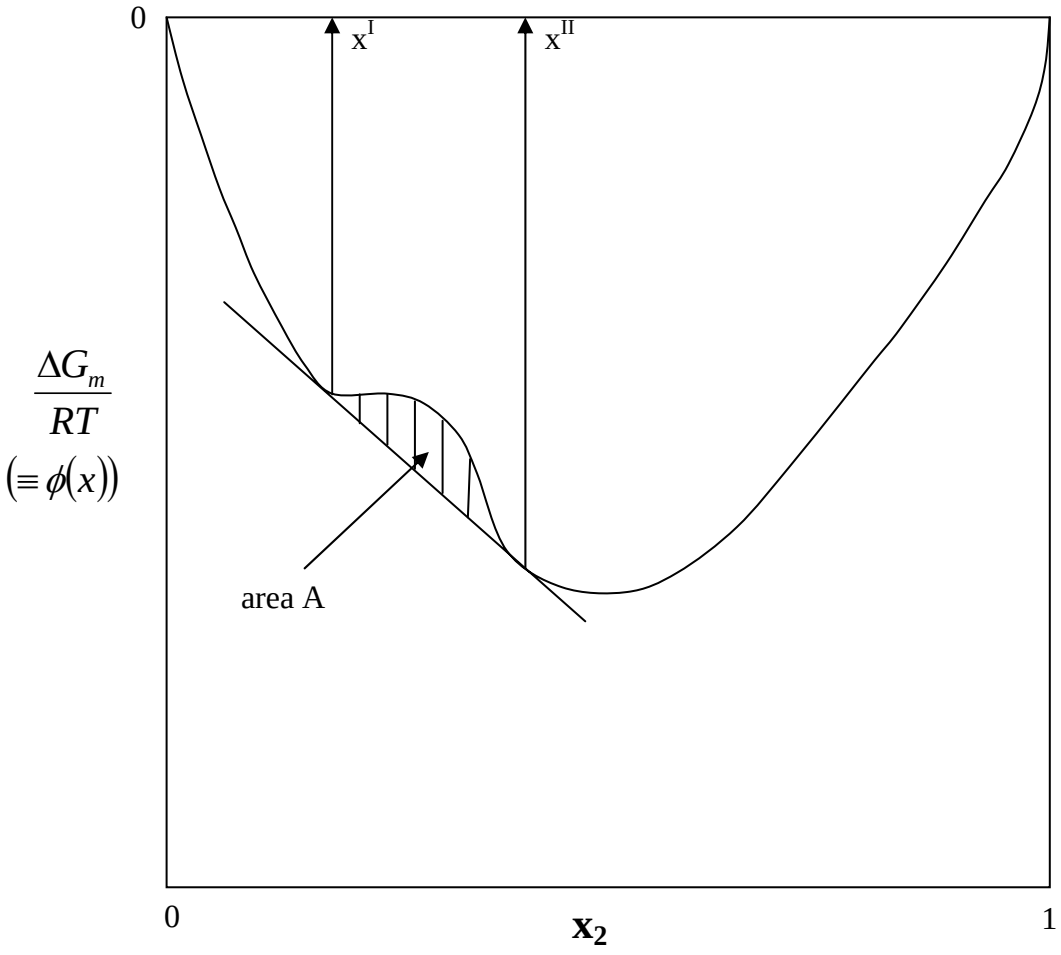


**Figure B.1**: Gibbs Energy of Mixing Curve for a Binary Mixture Forming Two Phases at Fixed Temperature and Pressure

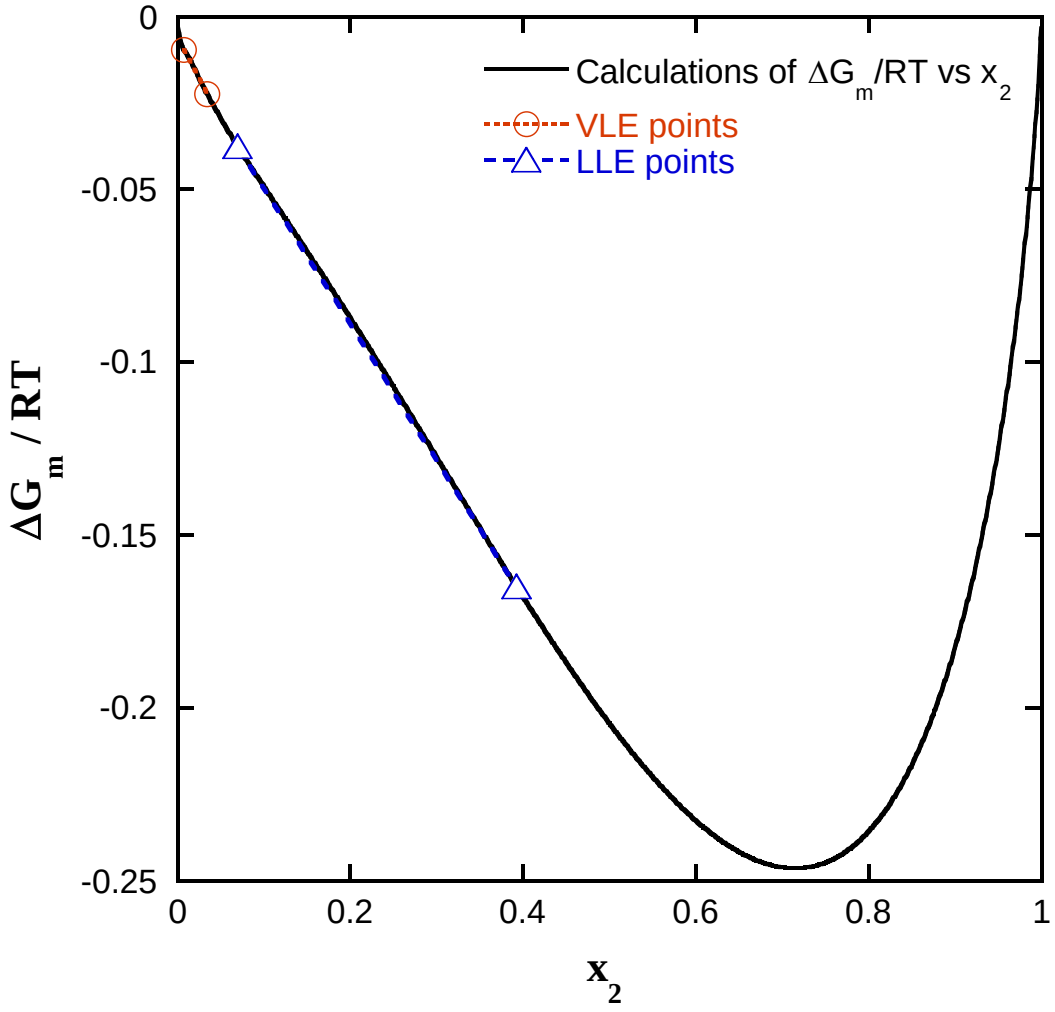


**Figure B.2**: Gibbs Energy of Mixing - Pyrrole Mole Fraction Curve at 313 K, 82 bar. Correlated with PT EOS + MKP Mixing Rule ($k_{12}$ =0.086, $l_{12}$ =0.045).

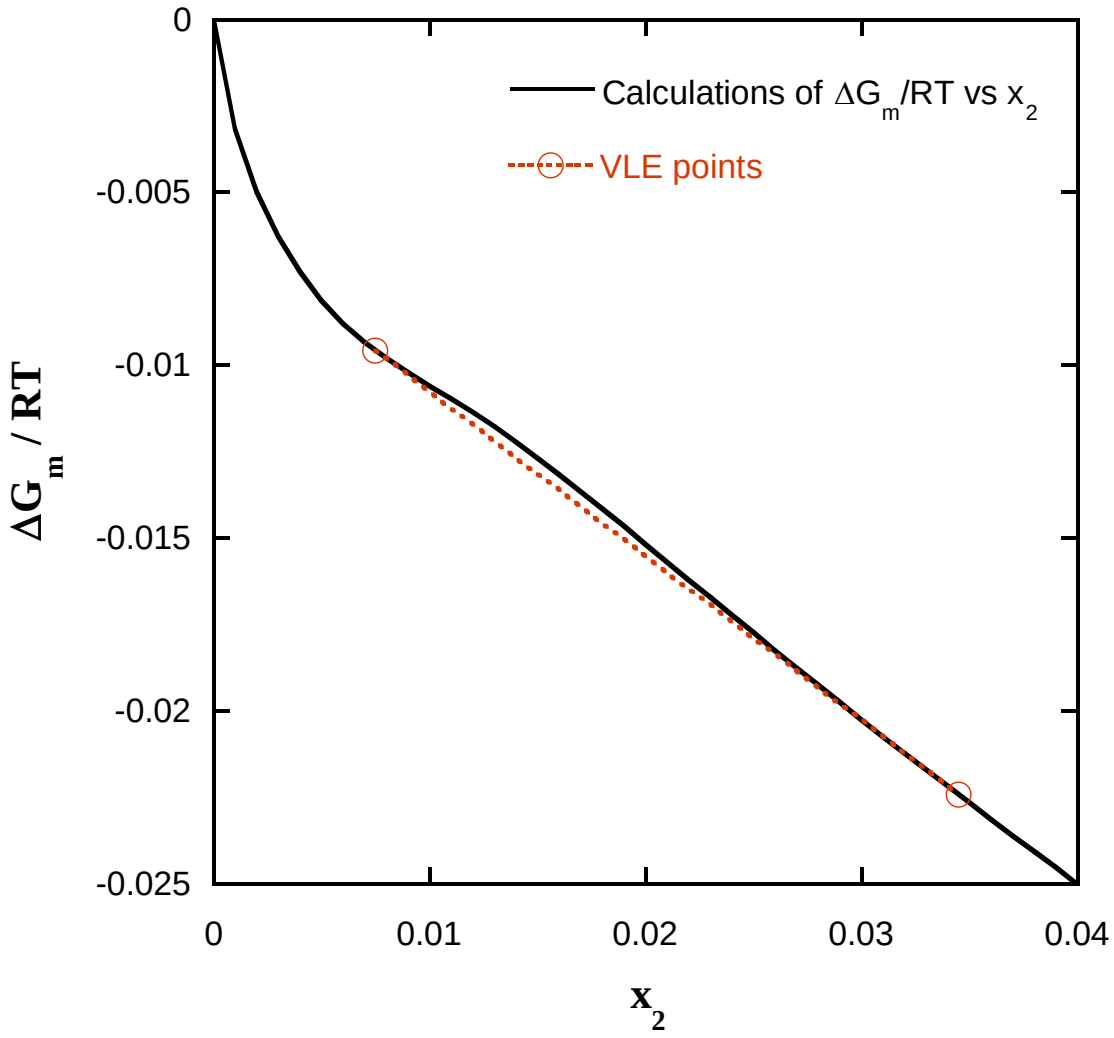


**Figure B.3**: The Enlarged Plot of Gibbs Energy of Mixing in the Low Pyrrole Mole Fraction Range at 313 K, 82 bar. Correlated with PT EOS + MKP Mixing Rule ($k_{12}$ =0.086, $l_{12}$ =0.045).

## REFERENCES


Abbett, K. F., Teja, A. S., Kowalik, J., and Tolbert, L. (2003a). "Polymerization of 3-Undecylbithiophene and preparation of Poly(3-undecylbithiphene)/Polystyrene Composites in Supercritical Carbon Dioxide." *Macromolecules*, 36(9), 3015-3019.

Abbett, K. F., Teja, A. S., Kowalik, J., and Tolbert, L. (2003b). "Preparation of conducting composites of polypyrrole using supercritical carbon dioxide." *Journal of Applied Polymer Science*, 90(4), 1113-1116.

Abedi, S. J., Cai, H. Y., Seyfaie, S., and Shaw, J. M. (1999). "Simultaneous phase behavior, elemental composition and density measurement using X-ray imaging." *Fluid Phase Equilibria*, 158-160, 775-781.

Abovsky, V., and Watanasiri, S. (1999). "Equation of state mixing rule based on activity coefficient model: explicit solution for ‘finite pressure approach'." *Fluid Phase Equlibria*, 158-160, 259-269.

Adachi, Y., and Sugie, H. (1986). "A new mixing rule - Modified conventional mixing rule." *Fluid Phase Equilibria*, 28(2), 103-18.

Arai, Y., Sako, T., and Takebayashi, Y. (2002). "Supercritical Fluids: Molecular interactions, Physical Properties, and New Applications." *Springer*, Germany.

Beier, A., Kuranov, J., Stephan, K., and Hasse, H. (2003). "High-Pressure Phase Equilibria of Carbon Dioxide + 1-Hexanol at 303..15 and 313.15 K." *Journal of Chemical and Engineering Data*, 48(6), 1365-1367.

Boublik, T. (1981). "Statistical thermodynamics of nonspherical molecule fluids." *Berrichte Der Bunsen-Gesellschaft-Physical Chemistry Chemical Physics*, 85, 1038-1041.

Byun, H.-S., and Kwak, C. (2002). "High pressure phase behavior for carbon dioxide-1-butanol and carbon dioxide-1-octanol systems." *Korean Journal of Chemical Engineering*, 19(6), 1007-1013.

Carnahan, N. F., and Starling, K. E. (1969). "Equation of state for nonattracting rigid spheres." *Journal of Chemical Physics*, 51, 635-636.

Carnahan, N. F., and Starling, K. E. (1972). "Intermolecular repulsions and the equation of state for fluids." *AIChE Journal*, 18(6), 1184-1189.

Chapra, S. C., and Canale, R. P. (1998). *Numerical Methods for Engineers*, McGraw-Hill, Singapore.

Christov, M., and Dohrn, R. (2002). "High-pressure fluid phase equilibria Experimental methods and systems investigated (1994-1999)." *Fluid Phase Equilibria*, 202(1), 153-218.

Chylinski, K., and Gregorowicz, J. (1998). "Solubilities of (1-hexanol, or 1,2-hexanediol, or 2-hydroxypropanoic acid ethyl ester, or 2-hydroxyhexanoic acid ethyl ester) in supercritical CO2." *Journal of Chemical Thermodynamics*, 30(9), 1131-1140.

Cooper, A. I. (2000). "Polymer Synthesis and Processing Using Supercritical Carbon Dioxide." *Journal of Materials Chemistry*, 10, 207-234.

Costa, M. A. M., Matos, H. A. S., Nunes da Ponte, M., and Gomes de Azevedo, E. J. S. (1996). "Binary and Ternary Phase Behavior of a-Pinene, b-Pinene, and Supercritical Ethene." *Journal of Chemical and Engineering Data*, 41(5), 1104-1110.

Dahl, S., and Michelsen, M. L. (1990). "High-pressure vapor-liquid equilibrium with a UNIFAC-based equation of state." *AIChE Journal*, 36, 1829-1836.

Dandge, D. K., Heller, J. P., and Wilson, K. V. (1985). "Structure solubility correlations: organic compounds and dense carbon dioxide binary systems." *Industrial and Engineering Chemistry Product Research and Development*, 24, 162-166.

Debelak, K. A., Roth, J. A., and Wang, T. (2003). "Recovery of minerals in Martian soils via supercritical fluid extraction." *NASA Conference Publication*, 2003-212339(2002 Microgravity Materials Science Conference), 155-166.

DIPPR. (2003). "Thermophysical Properties Database.", Design Institute for Physical Properties, New York, NY.

Dohrn, R., and Brunner, G. (1995). "High-pressure fluid-phase equilibria: experimental methods and systems investigated (1988-1993)." *Fluid Phase Equilibria*, 106(1-2), 213-82.

Eubank, P. T., Elhassan, A. E., Barrufet, M. A., and Whiting, W. B. (1992). "Area method for prediction of fluid-phase equilibria." *Industrial & Engineering Chemistry Research*, 31(3), 942-9.

Fall, D. J., and Luks, K. D. (1985). "Liquid-liquid-vapor phase equilibria of the binary system carbon dioxide + n-tridecane." *Journal of Chemical and Engineering Data*, 30, 276-279.

Firouzi, F., Modarress, H., and Ali Mansoori, G. (1998). "Predicting liquid-liquid transitions in polymer solutions using the GCLF equation of state." *European Polymer Journal*, 34(10), 1489-1498.

Fornari, R. E., Alessi, P., and Kikic, I. (1990). "High pressure fluid phase equilibria: experimental methods and systems investigated (1978-1987)." *Fluid Phase Equilibria*, 57(1-2), 1-33.

Fotouh, K., and Shukla, K. (1996). "A comparative study of numerical methods for calculating phase equilibria in fluid mixtures from an equation of state." *Chemical Engineering Science*, 51(15), 3763-3771.

Gibbons, R. M., and Laughton, A. P. (1984). "An equation of state for polar and nonpolar substances and mixtures." *Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics*, 80(9), 1019-38.

Guggenheim, E. A. (1965). "Variations on van der Waals equation of state for high densities." *Molecular Physics*, 9, 199-200.

Haruki, M., Iwai, Y., Nagao, S., Yahiro, Y., and Arai, Y. (2000). "Measurement and Correlation of Phase Equilibria for Water + Hydrocarbon Systems near the Critical Temperature and Pressure of Water." *Industrial & Engineering Chemistry Research*, 39(12), 4516-4520.

Heidemann, R. A., and Kokal, S. L. (1990). "Combined excess free energy models and equations of state." *Fluid Phase Equilibria*, 56, 17-37.

Hodges, D., Pritchard, D. W., and Anwar, M. M. (1995). "Liquid-liquid equilibria prediction using the area method." *Fluid Phase Equilibria*, 111, 27-36.

Hoelscher, I. F., Spee, M., and Schneider, G. M. (1989). "Fluid-phase equilibria of binary and ternary mixtures of carbon dioxide with hexadecane, 1-dodecanol, 1-hexadecanol and 2-ethoxyethanol at 333.2 and 393.2 K and at pressures up to 33 MPa." *Fluid Phase Equilibria*, 49, 103-13.

Huron, M. J., and Vidal, I. (1979). "New mixing rules in simple equations of state for representing vapour-liquid equilbria of strongly nonideal mixtures." *Fluid Phase Equilibria*, 3, 255-271.

Ishihara, K., Tanaka, H., and Kato, M. (1998). "Phase equilibrium properties of ethane + methanol system at 298.15 K." *Fluid Phase Equilibria*, 144(1-2), 131-136.

Ishikawa, T., Chung, W. K., and Lu, B. C. Y. (1980). "A cubic perturbed, hard sphere equation of state for thermodynamic properties and vapor-liquid equilibrium calculations." *AIChE Journal*, 26(3), 372-8.

Jennings, D. W. (1991). "High Pressure Phase Equilibria and Supercritical Fluid Extraction Involving Carbon Dioxide Systems," Ph.D. thesis, Georgia Institute of Technology, Atlanta.

Jennings, D. W., Lee, R. J., and Teja, A. S. (1991). "Vapor-liquid equilibria in the carbon dioxide + ethanol and carbon dioxide + 1-butanol systems." *Journal of Chemical and Engineering Data*, 36(3), 303-307.

Kaiser, C. S., Rompp, H., and Schmidt, P. C. (2001). "Pharmaceutical applications of supercritical carbon dioxide." *Pharmazie*, 56(12), 907-926.

Kazarian, S. G., Brantley, N. H., and Eckert, C. A. (1999). "Dyeing to be clean: use supercritical carbon dioxide." *Chemtech*, 29(7), 36-41.

Kerton, F. M., Lawless, G. A., and Armes, S. P. (1997). "First example of a conducting polymer synthesized in supercritical fluids." *Journal of Materials Chemistry*, 7(10), 1965-1966.

Kirby, C. F., and McHugh, M. A. (1999). "Phase behavior of polymers in supercritical fluid solvents." *Chemical Reviews*, 99(2), 565-602.

Knudsen, K., Stenby, E. H., and Fredenslund, A. (1993). "A comprehensive comparison of mixing rules for calculation of phase equilibria in complex systems." *Fluid Phase Equilibria*, 82, 361-8.

Kodama, D., Miyazaki, J., Kato, M., and Sako, T. (2004). "High pressure phase equilibrium for ethylene + 1-propanol system at 283.65 K." *Fluid Phase Equilibria*, 219, 19-23.

Kohnstamm, P., and Reeders, J. C. (1913). "Phenomena of condensation in mixtures of carbonic acid and nitrobenzene in connection with double retrograde condensation." *Proc. Acad. Wetenschappen*, 14, 270-280.

Kolafa, J., and Nezbeda, I. (1994). "Lennard-Jones fluid: an accurate analytic and theoretically-based equation of state." *Fluid Phase Equilibria*, 100, 1-34.

Kuenen, J. P., and Robson, W. G. (1899). "On the mutual solubility of liquids - vapor-pressure and critical points." *Philosophical Magazine Series 5*, 148, 180-203.

Kurosawa, S. (2004). "Supercritical Processing of Electrically Conducting Polymers," Ph.D. Thesis, Georgia Institute of Technology, Atlanta.

Lam, D. H., Jangkamolkulchai, A., and Luks, K. D. (1990). "Liquid-Liquid-Vapor Phase Equilibrium Behavior of Certain Binary Carbon Dioxide + n-Alkanol Mixtures." *Fluid Phase Equilibria*, 60(1-2), 131-41.

Lazzaroni, M. J., Bush, D., Jones, R., Hallett, J. P., Liotta, C. L., and Eckert, C. A. (2004). "High-pressure phase equilibria of some carbon dioxide-organic-water systems." *Fluid Phase Equilibria*, 224, 143-154.

Leitner, W. (2003). "A greener solution." *Nature*, 423 (6943), 930-931.

Li, Y. H., Dillard, K. H., and Robinson, R. L. (1981). "Vapor-Liquid Phase Equilibrium for Carbon Dioxide-n-hexane at 40, 80, and 120 $^{o}$C." *Journal of Chemical and Engineering Data*, 26, 53.

Malijevsky, A., and Veverka, J. (1999). "New equations of state for pure and binary hard-sphere fluids." *Physical Chemistry Chemical Physics*, 1, 4267-4270.

Mathias, P. M. (1983). "A versatile phase equilibrium equation of state." *Industrial & Engineering Chemistry Process Design and Development*, 22(3), 385-91.

Mathias, P. M., and Copeman, T. W. (1983). "Extension of the Peng-Robinson equation of state to complex mixtures: evaluation of the various forms of the local composition concept." *Fluid Phase Equilibria*, 13, 91-108.

Mathias, P. M., Klotz, H. C., and Prausnitz, J. M. (1991). "Equation-of-state mixing rules for multicomponent mixtures: the problem of invariance." *Fluid Phase Equilibria*, 67, 31-44.

Matsuda, T., Ohashi, Y., Harada, T., Yanagihara, R., Nagasawa, T., and Nakamura, K. (2001). "Conversion of pyrrole to pyrrole-2-carboxylate by cells of Bacillus megaterium in supercritical CO2." *Chemical Communications (Cambridge, United Kingdom)*(21), 2194-2195.

Matsuda, T., Watanabe, K., Harada, T., and Nakamura, K. (2004). "Enzymatic reactions in supercritical CO2: carboxylation, asymmetric reduction and esterification." *Catalysis Today*, 96(3), 103-111.

McHugh, M., and Krukonis, V. (1994). *Supercritical Fluid Extraction*, Butterworth-Heinemann, Stoneham.

Melhem, G. A., Saini, R., and Goodwin, B. M. (1989). "A modified Peng-Robinson equation of state." *Fluid Phase Equilibria*, 47(2-3), 189-237.

Michelsen, M. L., and Kistenmacher, H. (1990). "On composition-dependent interaction coefficients." *Fluid Phase Equilibria*, 58, 229-230.

Mühlbauer, A. L., and Raal, J. D. (1991). "Measurement and thermodynamic interpretation of high-pressure vapour-liquid equilibria in the toluene-CO2 system." *Fluid Phase Equilibria*, 64, 213-236.

Mukhopadhyay, M. (2000). *Natural Extracts Using Supercritical Carbon Dioxide*, CRC Press.

Nakayama, T., Sagara, H., Arai, K., and Saito, S. (1987). "High pressure liquid---liquid equilibria for the system of water, ethanol and 1,1-difluoroethane at 323.2 K." *Fluid Phase Equilibria*, 38, 109-127.

Nasrifar, K., and Moshfeghian, M. (2001). "A new cubic equation of state for simple fluids: pure and mixture." *Fluid Phase Equilibria*, 190(1-2), 73-88.

Ng, H. J., and Robinson, D. B. (1978). "Equilibrium Phase Properties at the Toluene-Carbon Dioxide System." *Journal of Chemical and Engineering Data*, 23, 325.

Orbey, H., and Sandler, S. I. (1996). "Analysis of excess free energy based equations of state models." *AIChE Journal*, 42, 2327.

Panagiotopoulos, A. Z., and Reid, R. C. (1986). "New mixing rule for cubic equations of state for highly polar, asymmetric systems." *ACS Symposium Series*, 300(Equations State), 571-82.

Patel, N. C., and Teja, A. S. (1982). "A new cubic equation of state for fluids and fluid mixtures." *Chemical Engineering Science*, 37(3), 463-473.

Peng, D. Y., and Robinson, D. B. (1976). "A new two-constant equation of state." *Industrial and Engineering Chemistry Fundamentals*, 15, 59-64.

Pfohl, O., Avramova, P., and Brunner, G. (1997). "Two- and three-phase equilibria in systems containing benzene derivatives, carbon dioxide, and water at 373.15 K and 10-30 MPa." *Fluid Phase Equilibria*, 141(1-2), 179-206.

Pfohl, O., Pagel, A., and Brunner, G. (1999). "Phase equilibria in systems containing o-cresol, p-cresol, carbon dioxide, and ethanol at 323.15-473.15 K and 10-35 MPa." *Fluid Phase Equilibria*, 157(1), 53-79.

Poling, B. E., Prausnitz, J. M., and O'Connell, J. P. (2001). "The Properties of Gases and Liquids." Singapore.

Raal, J. D., and Muhlbauer, A. L. (1998). *Phase Equilibria Measurement and Computation*, Taylor&Francis, Washington.

Raeissi, S., Gauter, K., and Peters, C. J. (1998). "Fluid multiphase behavior in quasi-binary mixtures of carbon dioxide and certain 1-alkanols." *Fluid Phase Equilibria*, 147, 239-249.

Rowlinson, J. S. (1988). *J.D. van der Waals: On the Continuity of the Gaseous and the Liquid States*, North Holland, Amsterdam.

Rowlinson, J. S., and Swinton, F. L. (1982). *Liquids and Liquid Mixtures*, Butterworth-Scientific, Great Britain.

Ruiz, F., Marcilla, A., Ancheta, A. M., and Rico, C. (1986). "Liquid-liquid equilibrium of the three liquid phases at equilibrium system water-phosphoric acid-diisopropyl ether at 25 and 40 DegC." *Solvent Extraction and Ion Exchange*, 4(4), 789-802.

Sadus, R. J. (1993). "Influnce of combining rules and molecular shape on the high pressure phase equilibria of binary fluid mixtures." *Journal of Physical Chemistry*, 97, 1985-1992.

Sandler, S. I. (1994). *Models for Thermodynamics and Phase Equilibria Calculations*, Marcel Dekker, New York.

Scheffer, F. E. C., and Smittenberg, J. (1933). "Binary systems II." *Recueil des Travaux Chimiques des Pays-Bas et de la Belgique*, 52, 1-8.

Schwartzentruber, J., and Renon, H. (1989). "Extension of UNIFAC to High Pressure and Temperatures by the Use of a Cubic Equation of State." *Industrial and Engineering Chemistry Research*, 28, 1049-1055.

Scott, R. L. (1971). *Physical Chemistry, An Advanced Treatise, Vol.8A: Liquid State*, Academic Press, New York.

Scott, R. L., and van Konynenburg, P. H. (1970). "Static properties of solutions: van der Waals and related models for hydrocarbon mixtures." *Discussions of the Faraday Society*, 49, 87.

Sengers, J. V., Kayser, R. F., Peters, C. J., and White Jr, H. J. (2000). *Equations of State for Fluids and Fluid Mixtures*, Elsevier, Amsterdam.

Shimoyama, Y., Haruki, M., Iwai, Y., and Arai, Y. (2002). "Measurement and Prediction of Liquid-Liquid Equilibria for Water + Hexane + Hexadecane, Water + Toluene + Decane, and Water + Toluene + Ethylbenzene Ternary Systems at High Temperatures and Pressures." *Journal of Chemical and Engineering Data*, 47(5), 1232-1236.

Smith, V. S.(1995). "Solid-fluid equilibria in natural gas systems," Ph.D. thesis, Georgia Institute of Technology, Atlanta.

Soave, G. (1972a). "Equilibrium Constants From a Modified Redlich-Kwong Equation of State." *Chem. Eng. Sci.*, 27(1197-1203).

Soave, G. (1972b). "Equilibrium constants from a modified Redlich-Kwong equation of state." *Chemical Engineering Science*, 27(1197-1203).

Soave, G. (1992). "A new expression of q($\alpha$) for the modified Huron-Vidal method." *Fluid Phase Equilibria*, 72, 325.

Soave, G. S. (1979). "Application of a cubic equation of state to vapor-liquid equilibriums of systems containing polar compounds." *Institution of Chemical Engineers Symposium Series*, 56(Distillation, Vol. 1), 1 2/1-1 2/16.

Span, R., and Wagner, W. (1996). "A New Equation of State for Carbon Dioxide Covering the Fluid Region from the Triple-point Temperature to 1100 K at Pressure up to 800 MPa." *Journal of Physical and Chemical Reference Data*, 25, 1509-1596.

Stryjek, R., and Vera, J. H. (1986). "PRSV - an improved Peng-Robinson equation of state with new mixing rules for strongly nonideal mixtures." *Canadian Journal of Chemical Engineering*, 64(2), 334-40.

Sun, T., and Teja, A. S. (1998). "Vapor-liquid and solid-fluid equilibrium calculations using a Lennard-Jones equation of state." *Industrial & Engineering Chemistry Research*, 37(8), 3151-3158.

Suzuki, T., Tsuge, N., and Nagahama, K. (1991). "Solubilities of ethanol, 1-propanol, 2-propanol and 1-butanol in supercritical carbon dioxide at 313 K and 333 K." *Fluid Phase Equilibria*, 67, 213-226.

Tang, M., Wen, T.-Y., Du, T.-B., and Chen, Y.-P. (2002). "Synthesis of electrically conductive polypyrrole-polystyrene composites using supercritical carbon dioxide II. Effects of the doping conditions." *European Polymer Journal*, 39(1), 151-156.

Teja, A. S., and Eckert, C. A. (2000). "Commentary on Supercritical Fluids: Research and Applications." *Industrial & Engineering Chemistry Research*, 39(12), 4442-4444.

Tsuji, T., Tanaka, S., Hiaki, T., and Saito, R. (2004). "Measurements of bubble point pressure for CO2 + decane and CO2 + lubricating oil." *Fluid Phase Equilibria*, 219(1), 87-92.

Tsurumaki, S., and Tasaka, Y. (1995). "Manufacture of conducting polymer composition." (Mitsubishi Heavy Industries, Ltd., Japan). Application: JP JP, 5 pp.

Twu, C. H., and Coon, J. E. (1996). "CEOS/$A^E$ mixing rules constrained by the vdW mixing rule and the second virial coefficient." *AIChE Journal*, 42, 3212-3222.

Twu, C. H., Coon, J. E., and Cunningham, J. R. (1995a). "A new generalized alpha function for a cubic equation of state Part 1. Peng-Robinson equation." *Fluid Phase Equilibria*, 105(1), 49-59.

Twu, C. H., Coon, J. E., and Cunningham, J. R. (1995b). "A new generalized alpha function for a cubic equation of state Part 2. Redlich-Kwong equation." *Fluid Phase Equilibria*, 105(1), 61-9.

Twu, C. H., Sim, W. D., and Tassone, V. (2002a). "Getting a handle on advanced cubic equations of state." Chemical Engineering Progress, 58-65.

Twu, C. H., Sim, W. D., and Tassone, V. (2002b). "A versatile liquid activity model for SRK, PR and a new cubic equation of state TST." *Fluid Phase Equilibria*, 194-197, 385-399.

Valderrama, J. P. (2003). "The state of the cubic equatioins of state." *Industrial and Engineering Chemistry Research*, 42, 1603-1618.

Van Konynenburg, P. H., and Scott, R. L. (1980). "Critical lines and phase equilibria in binary van der Waals mixtures." *Philosophical Transactions of the Royal Society of London Series A-Mathematical Physical and Engineering Sciences*, 298, 495-540.

Vandana, V., and Teja, A. S. (1995). "Vapor-liquid equilibria in the carbon dioxide + 1-propanol system." *Journal of Chemical and Engineering Data*, 40(2), 459-61.

Wagner, Z., and Wichterle, I. (1987). "High-pressure vapour--liquid equilibrium in systems containing carbon dioxide, 1-hexene, and n-hexane." *Fluid Phase Equilibria*, 33, 109-123.

Wei, M. S.-W., Brown, T. S., Kidnay, A. J., and Sloan, E. D. (1995). "Vapor + liquid equilibria for the ternary system methane + ethane + carbon dioxide at 230 K and its constituent binaries at temperatures from 207 to 270 K." *Journal of Chemical and Engineering Data*, 40(4), 726-731.

Wei, Y. S., and Sadus, R. J. (2000). "Equations of state for the calculation of fluid-phase equilibria." *AIChE Journal*, 46(1), 169-196.

Wong, D. S. H., Orbey, H., and Sandler, S. I. (1992). "Equation of state mixing rule for nonideal mixtures using available activity coefficient model parameters and that allows extrapolation over large ranges of temperature and pressure." *Industrial and Engineering Chemistry Research*, 31, 2033-2039.

Wong, D. S. H., and Sandler, S. I. (1992). "A theoretically correct mixing rule for cubic equations of state." *AIChE Journal*, 38, 671-680.

Yu, Z. R., Rizvi, S. S. H., and Zollweg, J. A. (1992). "Phase equilibria of oleic acid, methyl oleate, and anhydrous milk fat in supercritical carbon dioxide." *Journal of Supercritical Fluids*, 5(2), 114-22.

Zhang, W., and Kiran, E. (2003). "(p,V,T) Behaviour and miscibility of (polysulfone+THF+carbon dioxide) at high pressures." *Journal of Chemical Thermodynamics*, 35(4), 605-624.

Zimmerman, A., and Keller, J. (1989). "VLE In the system water-ammonia-lithium bromide." *Fluid Phase Equilibria*, 53, 229-234.